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Explicitly correlated wavefunctions for multielectron diatomics

by

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"Multa minuta modis multis per inane videbis
Corpora misceri radiorum lumine in ipso
Et velut aeterno certamine proelia, pugnasque
Edere turmatim certantia: nec dare pausam,
Consiliis, et discidiis exercita crebris."

Lucretius, De Rerum Natura

"There are many natures which can never approach within a certain distance, and which when any irregular motive impels them towards contact, seem to start back from each other by some invincible repulsion."

Samuel Johnson, The Rambler

I gratefully acknowledge the advice and support given to me by Professor D.M. Bishop during the course of my studies. Sincere thanks go to Dr. G. Maroulis for his interest in the theory of this research. The staff of the University of Ottawa Computing Centre were an invaluable help. I am grateful to the Natural Sciences and Engineering Research Council for a Postgraduate Scholarship.

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Abstract

The use of explicitly correlated wavefunctions, containing simple expressions that involve the distances between two electrons, has had a long and successful history of applications to two-electron atoms and molecules. Although variational wavefunctions involving these distances are more difficult to calculate, the expansion of the eigenfunction of the electronic Hamiltonian operator in terms of these functions is much shorter than an expansion that does not involve them.

In this work, the reasons for the rapid convergence of explicitly correlated wavefunctions will be discussed , as it applies to atoms, diatomics, and more general systems. A brief survey will be given of the major methods for introducing explicit correlation into a wavefunction, and the restrictions that these methods have put on the form of the wavefunction. A more flexible basis set will be proposed, and its ability to represent the wavefunction of a diatomic will be discussed. A general method for the calculation of explicitly correlated wavefunctions for multielectron diatomics will be elaborated. The techniques required for performing the difficult computations that arise from the method will be presented. These techniques

involve novel methods of integral evaluation, storage, and handling.

Results of a calculation performed on the ground state of LiH will be presented, including the calculation of many properties. These properties include the potential energy curves, dipole and quadrupole moments, electric polarizabilities in the direction of the axis, and cusp derivatives, as well the expectation values of many operators.

The effect of explicit correlation on the wavefunction and the properties will be discussed, with the intention of studying how correlation can most efficiently be introduced into molecular wavefunctions.

Preface

All the properties of a quantum mechanical system can be calculated as long as the wavefunction is known. In a one-electron system, be it an atom or a molecule, wavefunctions are analytic or can be easily evaluated since the separation of the wavefunction into nuclear and electronic coordinates is an accurate approximation.

In a multi-electron system, the electronic wavefunction can be evaluated to great accuracy relatively easily, as long as the electronic coordinates can be separated. Such a wavefunction, expressed as a product of one-electron functions, is a Hartree wavefunction, or a Hartree-Fock wavefunction if spin coordinates are used and the wavefunction is antisymmetric to the interchange of electrons. The method usually used to approximate HF (HartreeFock) wavefunctions in terms of a finite basis of functions is the SCF (self-consistent field) method.

Unfortunately, this separation of the electronic wavefunction is not accurate enough. Experimentally measured energy differences can differ from those that could be predicted from HF functions by hundreds of percent.
This energy difference is defined as the correlation energy.

The most popular method of obtaining wavefunctions where the electronic coordinates are not separated is by using a linear combination of these antisymmetrized products of one-electron functions, known as the CI (configuration interaction) method. This linear combination converges very slowly in most cases.

The alternative presented in this work is the explicitly correlated wavefunction, where electronic coordinates are not separated and the functions in the basis include powers of the interelectronic distances. This method has in the past seldom been extended to systems of more than two electrons.

Chapter 1 will review the history of these wavefunctions Chapter 2 will deal with the theory behind the success of the method; Chapter 3 will discuss the types of functions that can be used in a basis, including the ones used in this work; Chapter 4 will present the methods used and the integrals required; Chapter 5 will show the methods of evaluating the integrals; Chapter 6 will show which properties can be evaluated; Chapter 7 will present the results of our calculation on LiH; Chapter 8 will summarize our conclusions.

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CHAPTER 1

A REVIEW OF EXPLICITLY CORRELATED WAVEFUNCTIONS

The Ground State of Helium

It was early in the development of quantum mechanics that wavefunctions containing the interelectronic distance r_{12} were first used[1] for the calculation of the electronic energy of the He ground state. In 1927, Slater proposed and used a wavefunction that contained a term of the type $\exp[-2(r_1+r_2) + r_{12}/2]$ in that part of the wavefunction where r_1 and r_2 are both small. Here, r_1 is the distance between the nucleus and electron 1 and r_{12} is the interelectronic distance.

The major impetus for correlated wavefunctions came soon afterwards with the work of Hylleraas in 1929. Only three terms of a correlated function were sufficient to obtain

---

[1] J.C. Slater, Phys. Rev. 31, 333 (1927); 32, 349 (1928)

nearly 97% of the correlation energy[2] for the ground state of the helium atom. The coordinate system which Hylleraas developed[3] to make a quickly convergent expansion of the He wavefunction is the s, t, u triple:

$$s = r_1 + r_2 , \quad t = r_1 - r_2 , \quad u = r_{12}$$

(equation 1)

These coordinates are now known as Hylleraas coordinates, and the explicit use of interelectronic distances in the wavefunction as the Hylleraas method. The concept of Hylleraas coordinates has also been extended to include terms that depend on the angle Φ between the vectors $\vec{r}_1$ and $\vec{r}_2$, although this coordinate is redundant. These terms are most often introduced as spherical harmonics (normalized or unnormalized)

$$Y_l^m(\theta, \Phi)$$

(equation 2)

having nonzero values for m. Terms of this type are useful for representing p orbitals. The wavefunctions used by Hylleraas, referred to as Hylleraas wavefunctions, were linear combinations of terms of the form:

---

[2] E. Hylleraas, Z. Physik 54 , 469 (1928)

[3] E. Hylleraas Rev. Mod. Phys. 35 , 421 (1963)

$e^{-\alpha s} s^i t^j u^k$

(equation 3)

where (i,j,k) are nonnegative integers. The spin function, for this as well as the other wavefunctions of the singlet states of He is $(\alpha\beta-\beta\alpha)$, with the electronic indices dropped. The exponential parameter α, as well as the linear coefficients were calculated variationally. Hylleraas wavefunctions also allow for scaling all coordinates by a constant factor, making this factor an additional variational parameter. This factor can be fixed so as to cause the wavefunction to obey the virial theorem. In the work of Hylleraas, this factor is fixed at unity.

The six-term Hylleraas wavefunction was later extended to 10 terms[4], 14 terms[5], 34 terms[6], and 125 terms[7], yielding progressively better energies (see table I).

Many other explicitly correlated coordinate systems have been used for the two-electron atom. Pekeris[8] noticed that the Hylleraas coordinates could not vary independently

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[4] S. Chandrasekhar, D. Elbert, and G. Herzberg, Phys. Rev. 91, 1172 (1953)

[5] S. Chandrasekhar and G. Herzberg, Phys. Rev. 98, 1050 (1955)

[6] T. Kinoshita, Phys. Rev. 105, 1490 (1957)
A. Thakkar, Phys. Rev. A 16 1740 (1977)

[7] H. M. A. Radi, Phys. Rev. A 12, 1137 (1975)

[8] C. L. Pekeris, Phys. Rev. 112, 1649 (1958)

because of the triangular condition:

$$s \geq u \geq |t|$$

Pekeris therefore used a different set of coordinates, known as perimetric coordinates, first introduced by Coolidge and James,[9] defined as:

$$u_1 = (-r_1 + r_2 + r_{12})k/2$$
$$u_2 = (r_1 - r_2 + r_{12})k/2$$
$$u_3 = (r_1 + r_2 - r_{12})k$$

(equation 4)

where k is a constant intended to make the wavefunction's exponential parameter equal to unity. The value of this constant can be shown[8] to be $2(-E)^{1/2}$, where E is the energy of the system. These coordinates can vary independently and take any nonnegative real value. The solution of the analytical expressions obtained when the wavefunction is expanded in terms of Laguerre polynomials gives close to 100% of the correlation energy. Recursion relationships considerably simplify the calculation of the variational coefficients, provided, of course, that a function made up of a linear combination of Laguerre polynomials can be a solution to the Schroedinger equation.

---

[9] A. S. Coolidge and H. M. James, Phys. Rev. 51, 855 (1937)

Whether or not this is so, especially near the cusps, the results obtained by this method are as accurate as experiment if not more so. The best Pekeris wavefunction is made up of 1078 terms of the type:

$$e^{-(u_1+u_2+u_3)/2} L_l(u_1) L_m(u_2) L_n(u_3)$$

(equation 5)

where the $L_l(u)$ are normalized Laguerre polynomials of order l. It was later pointed out by Wang[10] that perimetric coordinates do not exist for systems containing more than three particles.

Kinoshita[6] studied the Hylleraas expansion, and proved that a wavefunction made up of a linear combination of the product of powers of the Hylleraas coordinates is not able to furnish a formal solution to the Schroedinger equation at the "triple collision" of two electrons with the nucleus. He therefore replaced it by one that could, with the coordinates defined by

$s = r_1 + r_2$

$p = r_{12} / s$

$q = (r_2 - r_1) / r_{12}$

(equation 6)

and the wavefunction expanded as a linear combination of

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[10] P. Wang, J. Chem. Phys. 47 , 2229 (1967)

terms of the form

$$s^{l} p^{m} q^{n} e^{-1/2 s}$$ (equation 7)

Kinoshita's method made the distinction between the lowest-energy wavefunction and the one having the greatest overlap with the exact lowest-energy eigenfunction of the Hamiltonian operator. His lowest energy for a 39-term wavefunction is -2.9037225 hartree. Kinoshita gave recurrence relations between only a few of the coefficients of the expansion. Explicit relations between all coefficients have been derived[11] for the 1^1S ground state of two-electron atoms. In this case, however, no calculation was performed.

Scherr also showed that some new restrictions had to be placed on the expansion, in particular restricting the exponent of s to nonnegative integer values and keeping $m \geq n$. This last condition is equivalent to restricting r_{12} to positive powers in the Hylleraas wavefunction. The same result[12] has been obtained by Tatum, using arguments of continuity of the wavefunction at the $r_{12} = 0$ cusp.

---

[11] C.W. Scherr Phys. Rev. A 19 469 (1979)

[12] J.P. Tatum, Int. J. Quantum Chem. 20 ,717 (1981)

Another set of correlated coordinates which has been used for the ground state of He is due to Munschy and Pluvinage[13] Their coordinates were:

$$u_1 = k(r_1 + r_2)$$
$$u_2 = r_{12} / (r_1 + r_2)$$
$$u_3 = (r_1 - r_2) / (r_1 + r_2)$$

(equation 8)

where k is, once again, equal to $2(-E)^{1/2}$, E being the energy of the system.

Other variations on the Hylleraas method are worthy of mention. In an effort to obtain the energies of Pekeris functions with fewer terms, half-integral[14] powers of the coordinate r_{12} were used in a wavefunction with some success, as well as half-integer[15] powers of s, where s = $(r_1 + r_2)$. Some very compact functions have been obtained by Frankowski and Pekeris[16] using terms in the wavefunction that augment the Hylleraas expansion by adding terms also involving powers of $(s^2 + t^2)^{1/2}$ and of ln(s), and some negative powers of s, where (s, t, u) are the Hylleraas

---

[13] G. Munschy and P. Pluvinage, Rev. Mod. Phys. 35, 494 (1963)

[14] H.M. Schwartz, Phys. Rev. 120, 483 (1960)

[15] C. Schwartz, Phys. Rev. 128, 1146 (1962)

[16] K. Frankowski and C.L. Pekeris, Phys. Rev. 146, 46 (1966)

coordinates. This wavefunction is also very accurate,[17] and in fact the lowest-energy wavefunction[18] published to date is a variation on this one, without the terms in $(s^2+t^2)^{1/2}$ and with more negative powers of s allowed in the expansion. Very compact as well is the wavefunction of Thakkar and Smith[19], which involves only exponentials of the Hylleraas coordinates, with optimized nonlinear parameters.

---

[17] K. Frankowski and C. L. Pekeris, Phys. Rev. 150, 366E (1966)

[18] D. E. Freund et al., Phys. Rev. A 29, 980 (1984)

[19] A. J. Thakkar and V. H. Smith, Jr., Phys. Rev. A 15, 1 (1977); 15, 16 (1977)

TABLE I

Variational, explicitly correlated wavefunctions for the 1^1S state of helium

reference	no. of terms	type of terms	energy	%correlation
2	2	Hylleraas	-2.89112	70.0
4	6	Hylleraas	-2.90324	98.85
4	10	Hylleraas	-2.9036014	99.71
5	14	Hylleraas	-2.9037006	99.95
6	39	Kinoshita	-2.9037225	99.995
7	125	Hylleraas	-2.903724371	99.99999
14	189	$r_{12}^{1/2}$	-2.90372437616	100.
8	1078	Pekeris	-2.903724376	100.
16	59	Frankowski&Pekeris	-2.903724351	99.99994
17	246	" "	-2.9037243770326	
18	230	ln(s)	-2.9037243770340	

Multi-electron Atoms

Given its success in obtaining a good energy for the ground state of He, the Hylleraas method was soon applied to other atoms. Two early pioneers in the field of explicitly correlated wavefunctions, Hubert James and Albert Sprague Coolidge, after having applied the Hylleraas method to the first excited state of helium,[20] performed a calculation on the ground state of the 3-electron Li atom,[21] using a Hylleraas-type wavefunction. The wavefunction they used was a 10-term expansion that included terms of the form:

$$e^{[-3(r_1+r_2) - \gamma r_3]}(r_1^i r_2^j r_3^k r_{23}^l r_{13}^m r_{12}^n)$$

(equation 9)

where (r_1, r_2, r_3), and (r_{23}, r_{13}, r_{12}) are defined as before as the distances of each of the three electrons from the nucleus and the three interelectronic distances,

---

[20] A.S. Coolidge and H.M. James, Phys. Rev. 49, 676 (1936)

[21] H.M. James and A.S. Coolidge, Phys. Rev. 47, 700 (1935) and 49, 688 (1936)

respectively. For some configurations, the second nonlinear parameter, γ, was 0.65, while for others the value 1.5 was used. The parameters i, j, k, l, m, n took on values of 0, 1, and 2, but a given term contained at most one nonzero power of an interelectronic distance. The use of terms involving more than one nonzero power of an interelectronic distance produces integrals that are difficult to evaluate.

In choosing their nonlinear parameters, James and Coolidge based themselves on the earlier work of Wilson[22], whose simple two-term wavefunction with a split outer shell had succeeded in giving a remarkably good energy of -7.4192 hartree. The energy for the James and Coolidge's 10-term Hylleraas-type wavefunction was -7.476075 hartree, compared with the experimental value estimated at -7.478069 hartree[23] or -7.478073 hartree.[24]

The problem of evaluating atomic integrals containing powers of the interelectronic coordinates was solved by Öhrn and Nordling.[25] Their methods were successfully applied by

---

[22] E.B. Wilson, Jr., J. Chem. Phys. 1 ,210 (1933)

[23] C.W. Scherr, J.N. Silverman, and F.A. Matsen, Phys. Rev. 127 ,830 (1962)

[24] C.F. Bunge, Phys. Rev. A 16 ,2496 (1977)

[25] Y. Öhrn and J. Nordling J. Chem. Phys. 39 ,

Larsson[26] to the $^2S_{1/2}$ state of Li, as well as other S states[27] and P states[28] of Li.

The integrands involving powers of the interelectronic coordinates are expanded in terms of spherical polar coordinates using a generalization of the Laplace expansion due to Sack[29]. The Sack expansion which seems easiest to use contains powers of the quotient $(r_< / r_>)$, where $r_<$ and $r_>$ represent the smaller and the larger of the pair (r_1, r_2) respectively. This makes it necessary to split expressions involving powers of the interelectronic coordinates into the half-spaces $(r_1 < r_2)$ and $(r_2 < r_1)$. Further breaking down is necessary for expressions involving powers of different interelectronic coordinates.

The Sack expansion has a finite number of terms when the power of the interelectronic coordinate is odd and positive or equal to -1. For even positive powers, the expansion contains an infinite series. It converges quickly enough that it can be truncated without significant losses in

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1864 (1963)

[26] S. Larsson, Phys. Rev. 169 , 49 (1968)

[27] S. Larsson, Phys. Rev. A 6 , 1786 (1972)

[28] T. Ahlenius and S. Larsson, Phys. Rev. A 8 , 1 (1973)

[29] R. A. Sack, J. Math. Phys. 5 , 245 (1964)

accuracy. Sack has also proposed[30] a more general formulation which is symmetric in r_1 and r_2, but this expansion is an infinite series and may not have the same convergence properties.

The integrals produced in Larsson's work are three types of relatively simple single, double, and triple integrals that can be evaluated to arbitrary precision analytically and by recursion.

The space part of the Larsson wavefunction was made up of a linear combination of terms of the type:

$$e^{[-\alpha(r_1+r_2) - \gamma r_3]}(r_1^i r_2^j r_3^k r_{23}^l r_{13}^m r_{12}^n) \qquad \text{(equation 10)}$$

The exponential parameters are constant for every term in the wavefunction. Only one power of the interelectronic coordinates is allowed to be nonzero in any given term. The powers (i, j, k, l, m, n) take on integer values in the range [0, 6]. The nonlinear parameters, of which there are only two, take on the partially optimized values of $\alpha=2.76$ and $\gamma=0.65$. It is interesting to note how little these exponential parameters differ from those of James and Coolidge.[21]

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[30] R. A. Sack, J. Math. Phys. 5, 252 (1964)

In his Li wavefunction, Larsson made use of the two linearly independent 3-electron spin functions which together span the space of functions having the correct S^2 and S_z eigenvalues for a state of symmetry $^2S_{1/2}$. These two spin functions are

$$\chi_1 = (\alpha\beta\alpha - \beta\alpha\alpha)$$
$$\chi_2 = (2\alpha\alpha\beta - \beta\alpha\alpha - \alpha\beta\alpha)$$

(equation 11)

where the electron indices are assumed.

Matrix elements involving the second spin function require very little additional computation, since the integration over the space coordinates does not change and the integration over the spin coordinates is trivial. The calculation is further simplified by the fact that all integrals involving the antisymmetrized product of the second spin function χ_2 and a function of the space coordinates which is symmetric in electrons 1 and 2 will be identically zero. Some additional computation is necessary because of the fact that a secular matrix equation of greater dimension must be solved when two different spin functions are included.

Including a term where the second spin function is multiplied by the space function:

$$\Phi_1(1)\Phi_2(2)\Phi_3(3) \qquad \text{(equation 12)}$$

is the same as having a term where the first spin function is multiplied by the space function:

$$\Phi_3(1)\Phi_2(2)\Phi_1(3) \qquad \text{(equation 13)}$$

Since the orbital exponents of Φ_1 and Φ_3 are quite different, this exchange between the inner and the outer shell will improve the radial dependence of both, as well as recovering some of the interelectronic correlation in that region of configuration space where the two orbitals overlap. It is quite possible to arrive at the same wavefunction without using the second spin function at all.

It can be argued that the second spin function is superfluous, since a 100-term wavefunction using both spin functions has an energy lower than that of the corresponding 60-term one-spin-function wavefunction by only 15 μhartrees. It must be pointed out, however, that the previous 15 terms in the 60-term function have contributed only 8 μhartrees to the energy. Although 15 μhartrees may not sound significant, the number of additional basis functions required to recover that energy using only one spin function may well be considerable, especially in light of the fact that no additional computational effort is necessary for the second spin function. Larsson and

Smith[31] have also demonstrated how the core-valence correlation introduced by the presence of the second spin function improves the description of observables such as the Fermi contact term.

Two of the terms included in Larsson's wavefunction involve two different interelectronic distances, where two of the three powers (l, m, n) in equation 10 are not zero. The contribution of these terms to the energy seems to be of the order of 20 μhartree. The inclusion of these terms is significant, since most other work on multielectron systems does not include explicit three-electron terms. It is generally assumed that the correlation between an electron and a pair of electrons separated by a small distance is taken into account by the spin function, since the third electron will be of the same spin as at least one of the other two electrons. It will not be able to occupy the same position as another electron with like spin, and the continuity of the wavefunction will therefore make it less likely to occupy a position in the same region of space.

The 100-term scaled wavefunction gave an energy of -7.478069 hartree (99.9% of the correlation energy). Parts of the calculation have been reproduced by Perkins,[32]

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[31] S. Larsson and V.H. Smith, Jr., Phys. Rev. 178, 137 (1969)

Ho[33], and in this laboratory[34]. Ho used a 92-term one-spin-function wavefunction to obtain a slightly better energy of -7.478031 hartree. The nonlinear parameters used in this calculation as well as that of Perkins are slightly different from those of Larsson, which were $\alpha=2.80$ and $\gamma=0.65$. These parameters have not in fact been optimized, but do give an energy lower by 10^{-6} hartree compared to the Larsson values for a 60-term wavefunction. It is interesting to note how little these differ from the Wilson parameters[11] of 1933, $\alpha=2.69$, $\gamma=0.65$, and those, cited by Wilson, used in the earlier work of Slater, and Guillemin and Zener, $\alpha=2.688$, $\gamma=0.63$.

The lowest variational energies for the 2^2S and 2^2P states of lithium[35] as well as for other states in the lithium isoelectronic sequence[36] have been obtained using the superposition of correlated configurations approach, a method very similar to the CI-Hylleraas method.

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[32] J. F. Perkins, Phys. Rev. A 13, 915 (1976)

[33] Y. K. Ho, Int. J. Quantum Chem. 20, 1077 (1981)

[34] D. M Bishop, M. Laplante, (unpublished results)

[35] J. Muszynska, D. Papierowska, and W. Woznicki, Chem. Phys. Lett. 76, 136 (1980)

[36] J. Pipin and W. Woznicki, Chem. Phys. Lett. 95, 392 (1983)

In this case, the energy obtained for the ground state of Li, using a 139-term expansion that included at most one interelectronic distance per term, raised to a power ranging from 0 to 3, with some terms having angular dependence, and two spin functions, was -7.478044 hartree. The exponents were optimized to $\alpha = 3.03$, $\gamma = 0.69$ for orbitals of s symmetry and 3.22 for orbitals of p symmetry.

The Hylleraas method has been used for four-electron atoms such as Be, most notably by Sims and Hagstrom.[37] Sims and Hagstrom use what they call the CI-Hylleraas method, where a product of four Slater type orbitals are multiplied by a power of one of the interelectronic coordinates. Each such configuration is combined with one of the two possible spin functions and operated on by the idempotent orbital angular momentum projection operator $O(L^2)$ to make it the appropriate eigenfunction of L^2. L^2, the square of the total angular momentum, is defined by

$$L^2 = L_x^2 + L_y^2 + L_z^2 \qquad \text{(equation 14)}$$

where the angular momentum operator is, in atomic units:

---

[37] J.S. Sims and S. Hagstrom, Phys. Rev. A 4, 908 (1971)

$$L_z = \frac{1}{i}(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})$$

(equation 15)

The method is an attempt to combine the best aspects of CI and Hylleraas-type expansions. The use of interelectronic coordinates, however, makes it impossible to use many simple CI methods, since orbitals containing such coordinates will not be orthogonal to the others.

The final wavefunction, using 107 configurations, was made up of s and p orbitals in both the core and the valence shell, and powers of all of the interelectronic coordinates taking values of (0,1,2). The energy obtained was -14.66654 hartree, compared to the estimated[38] limit of -14.667358 hartree, and a 650-term CI result of -14.666902 hartree. A more compact 57-term wavefunction[39] of the same type gave an energy of -14.66632 hartree. Calculations on Be are made more difficult by the near-degeneracy of 2s and 2p atomic orbitals. This near-degeneracy contributes to the importance of 'average' or long-range correlation, which can best be accounted for by a configuration interaction method, while the short-range Coulombic repulsion requires Hylleraas

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[38] C.F. Bunge, Phys. Rev. A 14, 1965 (1976); At. Data Nuc. Data Tables 18, 293 (1976)

[39] J.S. Sims and S.A. Hagstrom, Int. J. Quantum Chem. 9, 149 (1975)

terms[40]

Only one atom with more than four electrons has ever, to our knowledge, been treated by a Hylleraas wavefunction. A calculation on the ground state of neon[41] was performed by Clary and Handy, using the configuration interaction-Hylleraas method of Sims and Hagstrom. An 83-term wavefunction that included the first and second power of all interelectronic coordinates (no more than one per term) recovered 73.5% of the correlation energy of the atom. Although this is perhaps not as spectacular as Hylleraas-type calculations on smaller atoms, it compares very favorably with any CI approach[42] available at the time or since. When using a CI or even a pair expansion, the number of higher spherical harmonics necessary to recover the energy of angular correlation increases steadily with the number of electrons.[43] In fact, Bunge and Peixoto estimate that g, h, i,... orbitals are responsible for 8% of the

---

[40] J.W. Moskowitz et al., J. Chem. Phys. 76, 1064 (1982), R.E. Watson, Phys. Rev. 119, 170 (1960)

[41] D.C. Clary and N.C. Handy, Phys. Rev. A 14, 1607 (1976)

[42] C.F. Bunge and E.M.A. Peixoto, Phys. Rev. A 1, 1277 (1970)

[43] H.F. Schaefer III, The Electronic Structure of Atoms and Molecules (Addison-Wesley, Reading, Mass. 1972)

correlation energy and j, k, ... for 2%.

The hydrogen molecule

The H_2 molecule has, like He, had its history of successful calculations using the Hylleraas method of explicitly correlated wavefunctions. The earliest correlated wavefunction[44] due to James and Coolidge remained, for decades,[45] the best one available. Using elliptical coordinates defined by

$$\xi = (r_A + r_B)/R$$
$$\eta = (r_A - r_B)/R$$

(equation 16)

where r_A stands for the distance between an electron and the H nucleus labelled "A", as well as the additional interelectronic distance coordinate r_{12}, James and Coolidge built a wavefunction made up of a linear combination of terms of the type

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[44] H. James and A. Coolidge, J. Chem. Phys. 1, 825 (1933)

[45] for a 1960 bibliography, see A.D. McLean, A. Weiss, and M. Yoshimine, Rev. Mod. Phys. 32, 211 (1960)

$$e^{-\alpha(\xi_1+\xi_2)}(\xi_1^m\xi_2^n\eta_1^j\eta_2^k + \xi_1^n\xi_2^m\eta_1^k\eta_2^j)(2r_{12}/R)^p$$

(equation 17)

where α is a nonlinear variational parameter. This type of wavefunction, using products of orbitals, expressed in terms of elliptical coordinates, and powers of the interelectronic distance, are known as James-Coolidge wavefunctions. The use of "angular terms", in the form of

$$[(\xi^2-1)(1-\eta^2)]^{m/2}e^{im\phi}$$

(equation 18)

where ϕ is the angular coordinate in elliptical coordinates, m is an integer, and i is the square root of -1, is also possible in the wavefunction, although here again as was the case in spherical polar coordinates with atoms, ϕ is a redundant coordinate.

In order to represent the Σ ground state, the form of the wavefunction had to have the proper symmetry, invariant to rotation about the internuclear axis and to reflection in the plane of symmetry perpendicular to this axis. This implies the restriction of j+k even for the gerade ground state, or j+k odd in the case of the ungerade states. The conditions of antisymmetrization and spin are the same as in atomic wavefunctions. James and Coolidge, like most other subsequent authors using James-Coolidge wavefunctions, used only one value for α. The value they used was α=0.75 for both electrons. The energies calculated are summarized in table 2.

Using essentially the same form of the wavefunction, Kołos and Roothaan[46] extended the calculation to 50 terms, using a better-optimized value of $\alpha=0.95$. Further extensions of the same form of wavefunction were made by Kołos and Wolniewicz to 80 terms[47] and 100 terms[48] and by Bishop and Cheung to 249 terms[49] of the same type. In this largest calculation, and to some extent in some of the smaller ones, the best choice of basis functions is no longer done by trial-and-error and experience, but by including every possible basis function within a given range.

It should be noted that all the energies cited in table 2 correspond to Born-Oppenheimer energies at or near the equilibrium internuclear distance of 1.4 bohr, without radiative or relativistic corrections.

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[46] W. Kołos and C.C.J. Roothaan, Rev. Mod. Phys. 32, 219 (1960)

[47] W. Kołos and L. Wolniewicz, J. Chem. Phys., 41, 3674 (1964)

[48] W. Kołos and L. Wolniewicz, J. Chem. Phys., 49, 404 (1968)

[49] D.M. Bishop and L.M. Cheung, Phys. Rev. A 18, 1846 (1978)

TABLE II

Variational explicitly correlated wavefunctions for the $X^1\Sigma^+$ state of hydrogen

reference	no. of terms	value of α	energy	%correlation
44	5	0.75	-1.16645	80.4
44	13	0.75	-1.173475	97.6
46	50	0.95	-1.174448	99.93
47	80	1.0	-1.1744746	99.997
48	100	1.072	-1.1744749830	99.998
49	249	1.117	-1.17447565	100.

There is an extensive literature on the non-Born-Oppenheimer wavefunctions for small molecules[50] These

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[50] See, for instance, D.M. Bishop and L.M. Cheung, in "Advances in Quantum Chemistry", vol. 12, p. 1, ed. P.O. Löwdin, Academic Press, London, 1980, and references cited therein.

calculations do not assume that the electronic wavefunction can be separated from the nuclear wavefunction. Except in the case of the variational non-adiabatic calculations, these calculations give approximate values of the eigenvalues of the total Hamiltonian, rather than strict upper bounds to them.

Multielectronic molecules

The difficulties encountered in attempting to evaluate integrals involving interelectronic distances in elliptical coordinates have made variational calculations of explicitly correlated wavefunctions for multielectronic molecules rare. These integrals have been referred to variously as "difficult", "formidable", "horrific", and "almost intractable". This opinion was not dispelled when Rothstein[51] published an expansion in terms of elliptical coordinates of the integrals required to evaluate the Hamiltonian matrix elements for a wavefunction containing at most the first power of one of the interelectronic

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[51] E.V. Rothstein, Phys. Rev. A 3, 1581 (1971)

coordinates. With that restriction, each matrix element will involve at most three interelectronic terms (one from the bra, one from the ket, and a reciprocal interelectronic distance from the Hamiltonian) and at most four electrons. Rothstein classified each of the integrals into 10 distinct types, then expanded the reciprocal of the interelectronic coordinate according to the Neumann expansion (see chapter 4), and the first power of the coordinate according to the (unpublished until then) Harris expansion. A number of corrections to these equations have been published by Clary,[52] who used the same approach to calculate the first explicitly correlated wavefunctions for many-electron diatomic molecules.

For the three-electron molecule He_2^+, Clary's 29-term explicitly correlated wavefunction recovers about 90% of the correlation energy at the equilibrium internuclear distance for the lowest $^1\Sigma^+$ state of the molecule. The wavefunction used in this case is made up of a linear combination of products of three orbitals of the form:

$$\exp(-2.057\xi)[\exp(1.163\eta)+\exp(-1.163\eta)]\eta^i\xi^j \text{ , for g symmetry} \quad \text{(equation 19)}$$

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[52] D.C. Clary, Mol. Phys. 34 ,793 (1977)

$\exp(-1.890\xi)[\exp(1.765\eta)-\exp(-1.765\eta)]\eta^i\xi^j$, for u symmetry
(equation 20)

and a power of one of the interelectronic distances. The four nonlinear parameters for the different orbitals were optimized using a small basis set without explicitly correlated terms. The parameters i and j took on the values (0,1,2). Only three of the terms contained an interelectronic distance, to the first power, none of the terms had explicit angular dependence, and only one of the two possible singlet spin functions was used. That the energy obtained from this calculation is so low in spite of all these limitations speaks eloquently for the power of the method.

Clary performed a similar calculation on the weakly bound $^1\Sigma^+$ state of the He_2 "molecule" at the short internuclear distance of 1.0 bohr (not the equilibrium internuclear distance). The form of the wavefunction used is the four-electron analogue of the He_2^+ wavefunction discussed above. Three of the 34 terms used contain the first power of one of the internuclear distances r_{12}, r_{34}, and r_{13}, to account for what has come to be known as the "core", "valence", and "inter-shell" correlation, respectively.

The calculated energy of -4.88323 hartree obtained seems to be the lowest variational energy for the internuclear distance of one bohr. As in the previous calculation, two sets of exponents are used, one representing a gerade state and the other an ungerade state. Since the exponents are rather small at such a small internuclear distance, the correlation energy is easily recovered with a small correlated basis set.

The only explicitly correlated wavefunction to have been published so far for LiH (or any heteronuclear diatomic having more than two electrons, for that matter) is also due to Clary and Handy.[53] Using a 117-term wavefunction that included only two terms with the first power of r_{12} and r_{34} and what they called "poor" ground configurations, whose energy is far above the Hartree-Fock limit, 91% of the correlation energy was recovered at the equilibrium internuclear distance. A 24-term expansion[54] of "poor" orbitals gave 87% of the correlation. One set of nonlinear parameters was used for the core and two sets for the valence. Only one of the two possible spin functions was included. The correlated term providing for the "core-valence" correlation was not included in the final wavefunction because of its negligible contribution to the energy. This calculation compares

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[53] D.C. Clary and N.C. Handy, Chem. Phys. Lett. <u>51</u>, 483(1977)

[54] D.C. Clary, Ph.D. Thesis, University of Cambridge (1977)

favorably with much larger CI and other variational calculations of the energy.

When an expansion in terms of Hylleraas coordinates or a James-Coolidge function contains only even powers of the interelectronic distances, it is not generally considered an explicitly correlated wavefunction. This is because the square of the internuclear distance can be expressed, in spherical polar coordinates, as

$$r_{12}^2 = r_1^2 + r_2^2 - \frac{4\pi}{3} r_1 r_2 \sum_{m=-1}^{+1} Y_1^m(1)\, Y_1^{-m}(2)$$

(equation 21)

where the Y_1^m (i) are spherical harmonics, and in elliptical coordinates as a Neumann expansion (see chapter 4).

Whether in spherical polar or elliptical coordinates, any term containing an even power of the interelectronic distance can be expressed as a linear combination of "uncorrelated" terms some of which will have angular dependence. This expansion therefore reduces to something like a CI expansion.

Therefore, when the claim is made that Clary's is the only explicitly correlated wavefunction in the literature for the LiH molecule, we are excluding such wavefunctions as correlated spherical Gaussians[55] and correlated Gaussian geminals,[56] which involve only the second power of the interelectronic distances.

One method which is worth mentioning in this section, even though it has not yet, to our knowledge, been applied to a molecule with more than two electrons, is the polyatomic superposition of correlated configurations[57] method. The method in this case is similar to the Superposition of Correlated Configurations (SCC) and CI-Hylleraas methods discussed earlier, with the Slater orbitals being replaced by linear combinations of spherical gaussians centered at different points around the nuclei(Gaussian lobe functions). The complexity of the calculation apparently does not depend on the number of different centers used, so that polyatomic molecules can be treated using combinations of such orbital products, multiplied by powers of the interelectronic coordinates.

Only the two-electron $H_3{}^+$ molecule has been treated

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[55] K. M. Karunakaran and R. E. Christoffersen, Int. J. Quantum Chem. 21 , 1 (1982) and 21 , 11 (1982)

[56] S. F. Boys, Proc. Roy. Soc. A256 , 402 (1960)

[57] A. Preiskorn and W. Woznicki, Chem. Phys. Lett. 86, 369 (1982)

using this method. A 36-term explicitly correlated wavefunction recovered 94% of
the correlation energy of the lowest A_1' state at the equilibrium nuclear configuration. One presumes that the evaluation of multielectron integrals is the difficulty that must be resolved before calculations are possible on multielectronic molecules.

CHAPTER 2

CORRELATED WAVEFUNCTIONS AND INTERELECTRONIC CUSPS

The form of the Hamiltonian operator

When the familiar time-independent Hamiltonian operator

$$H = T + V$$

is a self-adjoint bounded linear operator defined in finite or infinite-dimensional Hilbert space, the spectral theorem allows that it have a spectral representation in that finite or infinite-dimensional space.[58] If the operator is defined on L^2, the space of square integrable functions on the real line, then the operator H will admit an eigenfunction expansion provided that the solutions ψ_n to the equation

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[58] J. M. Jauch, "Foundations of Quantum Mechanics", (Addison-Wesley, Reading) 1968

$H\psi_n = E_n\psi_n$

(equation 1)

can form a complete orthonormal system. These eigenfunctions can then form the basis for a matrix representation of the operator H in block diagonal form. The eigenvectors belonging to an eigenvalue E_n are a subspace of that Hilbert space with a dimension equal to the multiplicity of the eigenvalue. Since the matrix representation of the Hamiltonian in a Hilbert space is Hermitian, the eigenvalues will be real. By a unitary transformation on to another complete set, one can obtain eigenvectors in a particular coordinate system.

In practice, except for a few quantum mechanical systems, this transformation from the spectral representation in abstract Hilbert space to that described by a given finite-dimensional basis will be a projection onto a subspace. This is especially so when the distances of several particles are linked in the operator. Applying the Hamiltonian operator to a given function in this basis will not in general map it on to a new function which is contained entirely in this subspace. The Schroedinger equation will therefore not have solutions on this subspace unless the Hamiltonian operator is replaced by one which is projected onto the basis set. Let the basis set be $\Phi_1, \Phi_2,$

$\Phi_3, \ldots, \Phi_N$. The projection of the Hamiltonian[59] will then be

$$|\Phi_i\rangle\langle\Phi_j| H$$

(equation 2)

where the indices are summed over all possible values in the basis set. When one is determining the eigenfunction having the lowest eigenvalue, within the function space defined by a basis set, by the linear variational method, this wavefunction will be the one which maximizes the overlap between Ψ and $H\Psi$.

It has never been proven, even in the case of the helium atom that there exists any basis set of analytical functions, be it finite or infinite, which can provide a formal solution to the Schroedinger equation. Not until recently was a non-variational infinite series method shown[60] to be able to provide a formal solution to the Schroedinger equation that satisfies the boundary conditions at the nucleus and the normalizability condition. This solution derives from an infinite-order perturbation series with the electronic repulsion as the perturbing factor. In

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[59] J. Avery, "The Quantum Theory of Atoms, Molecules, and Photons", McGraw-Hill, London, 1972

[60] C.L. Davis, E.N. Maslen, J.N. Varghese, Proc. R. Soc. London Ser. A 384 , 57 (1982); C.L. Davies and E.N. Maslen, Int. J. Quantum Chem. Quantum Chemistry Symposium 17 217 (1983)

spite of the practical success of the Hylleraas expansion, it has been shown[61] that no wavefunction that can be expressed as a power series in r_1, r_2, and r_{12} can be a formal solution to the Schroedinger equation, and this result can be extended to the Hylleraas wavefunctions as well.

Bartlett elaborated,[62] following the calculations in a posthumous paper by Gronwall[63], on the form which the wavefunction can and cannot have in the region of the nuclear singularity, if it is to be a formal solution to the Schroedinger equation. More recently, it has been shown[64] that there can be no Frobenius series solution to the helium atom problem. The expansion of the wavefunction around the electronic and nuclear cusps for the lowest singlet S states of the helium isoelectronic series, as well as the explicit values of the first few terms in the expansion, was given by Fock[65] in 1954, and extended more recently by

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[61] J. H. Bartlett, Jr., J. J. Gibbons, Jr., C. G. Dunn, Phys. Rev. 47, 679 (1935)

[62] J. H. Bartlett, Jr., Phys. Rev. 51, 661 (1937)

[63] T. H. Gronwall, Phys. Rev. 51, 655 (1937)

[64] C. S. Withers, Phys. Rev. 30, 1506 (1984)

[65] V. A. Fock, Izv. Akad. Nouk SSSR Ser. Fiz. 18, 161 (1954)

Pluvinage[66] for other S states. The first few terms in such an expansion are:

$$\begin{aligned}\Phi_F = {} & 1 - Zr_1 - Zr_2 - (1/2)r_{12} + Z\, r_1^2 r_2 \\ & - (1/12)(2E-4Z^2-1)r_{12}^2 - (1/2)Zr_{12}(r_1+r_2) \\ & + \quad (r_1^2+r_2^2-r_{12}^2) - (1/6)Z(1-\mu) \\ & [(2-Zr_1-Zr_2+r_{12})(r_1^2+r_2^2-r_{12}^2)+(1/6)r_{12}^3] \\ & \ln[(r_1^2+r_2^2)^{1/2}] + \ldots\ldots \end{aligned}$$

(equation 3)

where E is the electronic energy, Z is the nuclear charge, and μ is an arbitrary parameter. The Kinoshita expansion, mentioned earlier, also has the property of being able to represent a formal solution of the Schroedinger equation in the vicinity of some of the nuclear and electronic cusps. The importance of this is demonstrated by the success of the Kinoshita expansion and other expansions based on the Fock expansion in obtaining a low energy for the helium ground state.

The fact that any particular expansion can be proved not to be capable of providing a formal solution to the Schroedinger equation may be considered a moot point when it comes to calculating eigenvalues and most expectation values. James and Coolidge have shown[9] that the Hylleraas expansion, even though it may not be able in an infinite

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[66] P. Pluvinage, J. Physique 43, 439 (1982)

series to represent the exact eigenfunction, can in a finite expansion give a wavefunction which is arbitrarily close to this eigenfunction, with an eigenvalue arbitrarily close to the exact eigenvalue.

In extending the expansion in terms of Hylleraas coordinates from a finite to an infinite series, some of the coefficients will diverge as an attempt is made to expand a discontinuity in terms of continuous functions. The derivative of the expansion at the cusp will be different from that of the exact wavefunction. However, since most observables are calculated by integrals over all space, the contribution of a single point to these integrals will be infinitesimal.

One can easily see intuitively[67], however, that if a finite expansion made up of continuous functions is incorrect at one point, then it will also be incorrect in the neighbourhood of that point. Still intuitively, then, the reason for the success of the Hylleraas expansion is its ability to give the correct value of the wavefunction in those parts of configuration space where $r_{12}=0$ and good values in the neighbourhood, and the reason for the greater

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[67] For a graphic illustration of this in the case of the hydrogen molecular ion, see A.C. Hurley, "Introduction to the Electron Theory of Small Molecules" (Academic Press, London and New York) 1976, p.59

success of wavefunctions based on the Kinoshita and Fock expansions is their ability to give the correct behaviour of the wavefunction and its derivatives at all cusps.

The size of the "neighbourhood" of the $r_{12}=0$ cusp that Hylleraas expansions represent has been a matter of some discussion. Using local energy methods, one can easily see that the local potential energy is infinite when $r_{12} = 0$ and very large when r_{12} is very small. A product of one-electron space functions multiplied by r_{12} will give a compensating infinite kinetic energy when r_{12} is 0 and compensate for the potential in the area of the cusp.

A function containing terms that are multiplied by the first power of the interelectronic coordinates will also be able to obey Kato's[68] equation for the derivative of the wavefunction with respect to the interelectronic distance near the singularity:

$$\left[\frac{1}{\psi}\frac{\partial\psi}{\partial r_{12}}\right]_{r_{12}=0} = 1/2$$

(equation 4)

When one goes further from this cusp, the shape of the so-called Coulomb hole[69] can no longer be represented by a

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[68] T. Kato, Commun. Pure Appl. Math. 10 , 151 (1957)

function that is linear in the interelectronic distance.

However, it has been argued by Gilbert[70] that the reason for the rapid convergence of correlated wavefunctions is not so much the short-range description of the cusp at $r_{12} = 0$ as the simplicity of the representation of a Coulomb hole that is spherical and of a radius similar to that of the atom as a rapidly convergent expansion in r_{12}. Gilbert supports his arguments with the fact that there is a nearly linear relation between the pair distribution function and the error in the energy[71]. In the case of the ground state of helium, he calculated how simple in fact was the structure of the Coulomb hole relative to one of the electrons, using published correlated wavefunctions. Almost independently of the electronic and interelectronic coordinates, the calculated Coulomb hole is smooth and nearly linear. Although Gilbert speculates that his analysis may not apply to orbitals with quantum numbers $n>1$ and $l>0$, further study shows[72] that the Coulomb hole

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[69] see, for instance, S. Manoli and M. A. Whitehead, Phys. Rev. A 23 , 2150 (1981) and the references cited in Cohen and Frishberg, Int. J. Quantum Chem. 23 , 249 (1983)

[70] T. L. Gilbert, Rev. Mod. Phys. 35 , 491 (1963)

[71] C. A. Coulson and A. H. Neilson, Proc. Phys. Soc. (Lon.) 78 , 831 (1961)

[72] see for instance He atom excited states K. E. Banyard and P. K. Youngman J. Phys. B 15 , 853 (1982); and

generally has the same simple structure.

Further evidence in support of this analysis comes from the use of cutoff correlation factors[73] in a wavefunction, where orbital products are multiplied by a correlation factor of the form:

$$g(r_{12}) = 1 + c\,h(r_{12}),$$

$$h(r_{12}) \begin{cases} = r_{12} & (0<r_{12}<D) \\ = D & (D<r_{12}) \end{cases}$$

(equation 5)

where c is a constant and D is the cutoff parameter. By seeing how the energy varies with D, one obtains the striking result that the derivative of the energy with respect to D is near zero as D gets small. This means that the effect on the energy of having correlation in the wavefunction in the immediate vicinity of the $r_{12}=0$ cusp is almost non-existent.

Let ΔE be the difference in energy between a wavefunction where D=0 and one where $D=\infty$. For one simple form of the wavefunction, only 5% of ΔE is recovered when

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Be atom in K. E. Banyard and R. J. Mebbs, J. Chem. Phys. 75, 3433 (1981)

[73] B. M. Gimarc, W. A. Cooney, and R. G. Parr, J. Chem. Phys. 42, 21 (1965)

D=0.3 bohr, 50% is recovered when D=1.0 bohr and 95% when D=2.0 bohr. When more complex forms of the wavefunction are used, the qualitative behaviour is about the same, but even larger cutoff factors are required.

The use of a function of a form such that it has the possibility to obey the cusp condition does not mean that it will approach the correct cusp behaviour variationally. It has been shown numerically by Tatum[12] that only very large flexible wavefunctions will tend variationally towards an approximately correct averaged derivative of the wavefunction at the r_{12} =0 cusp. In fact, those Kinoshita expansions which include a negative power of r_{12} will have a discontinuous derivative at the cusp, and still give a very low value for the energy. Wavefunctions found by the configuration interaction (CI) method, as well as those involving only even powers of the interelectronic distance will have identically zero derivatives at the cusp, rather than the correct value of 0.5.

A CI expansion still forms a complete set spanning the space of the eigenfunctions of the Hamiltonian operator[74] and can therefore give variational wavefunctions with eigenvalues that are arbitrarily close to the exact

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[74] P.O. Löwdin, Phys. Rev. 97 , 1474 (1955)

eigenvalues. The expansion of the eigenfunctions in terms of a CI basis set will be very long, however, because of the number of functions with higher angular momentum necessary to fit the angular correlation near the interelectronic cusps.[75]

A wavefunction can of course be constrained to obey the cusp condition for the first and higher derivatives, for example[76] by multiplying orbital products by the correlation factor

$$\prod_{ij} \sum_{n=0}^{\infty} \frac{r_{ij}^{n}}{n!(n+1)!}$$

(equation 6)

where r_{ij} is the distance between electrons i and j. A constrained function can not give a lower energy than a variational one.

The reasoning given by James and Coolidge for their choice of correlated functions in their wavefunction for the first excited state of He may give some insight into the problem of long-range versus short-range correlation effects of Hylleraas expansions. James and Coolidge considered what should be the difference between a variational wavefunction

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[75] C. Schwartz, Phys. Rev. 126 , 1015 (1962)

[76] H. Conroy, J. Chem. Phys., 41 , 1327 (1964), and 41 , 1341 (1964)

made from a basis set independent of interelectronic distance and one made from the same basis set augmented by the first power of the interelectronic distance. Calling the first wavefunction ψ_R, they reason that an approximate correlated wavefunction ψ_C can be approximated by the relation:

$$\psi_C = 1 + c[1/r_{12} - 1/g(1,2)] \quad \psi_R \qquad \text{(equation 7)}$$

where c is a constant and g(1,2) is the effective interelectronic distance in an uncorrelated wavefunction, approximated as the greater of r_1 and r_2. The reciprocal of g(1,2) may be considered as the effective interelectronic potential for uncorrelated wavefunctions. Multiplying the expression by the approximate equation

$$r_{12}/g(1,2) \doteq 1 \qquad \text{(equation 8)}$$

we obtain

$$\begin{aligned} \psi_C &\doteq 1 + c[1/g(1,2) - r_{12}/g(1,2)^2] \quad \psi_R \\ &\doteq 1 + c[r_>^{-1} - r_>^{-2}\, r_{12}] \quad \psi_R \end{aligned} \qquad \text{(equation 9)}$$

where $r_>$ is r_1 or r_2, whichever occupies the more diffuse orbital.

The essence of the argument is that terms that can be expressed as an orbital product multiplied by an interelectronic distance must be used in conjunction with terms having the same orbital product multiplied by the greater of r_1 and r_2, as well as the square of this distance, especially when this last term is an important one in the uncorrelated wavefunction. Another way of putting it is to say that for large values of r_1, the variable r_{12} will behave like r_1. To correct this "undesirable" dependence on r_{12} for large r_1 (and therefore large average r_{12}), the wavefunction must be made more flexible in r_1 than it need have been in the absence of explicitly correlated terms. Long-distance and short-distance correlation can therefore not easily be separated in Hylleraas coordinates, since a variational wavefunction that has the correct behaviour at large interelectronic distances can be made worse at these large distances by the addition of explicitly correlated terms intended to improve the wavefunction for short interelectronic distances.

CHAPTER 3

James-Coolidge wavefunctions for many-electron diatomics

The success of James-Coolidge wavefunctions in 2-electron calculations made them natural candidates for extension to larger systems, if the computational difficulties can be overcome. The advantages of this approach included, besides the accurate description of electronic correlation, the elimination of atomic bias by the use of elliptical rather than LCAO (linear combination of atomic orbitals) orbitals, the flexibility of the wavefunction, allowing expansions that are not in terms of eigenfunctions of approximate Hamiltonian operators, expandability of the wavefunction, allowing for the convergence properties to be investigated by systematically raising the different indices defining the basis functions, and the independence of the form of the explicitly correlated terms from the terms not explicitly correlated.

Parts of their approach have been used successfully in many-electron diatomics, and most notably in LiH calculations. In 1936, Knipp[77] used an interesting wavefunction in a calculation of the energies of LiH and LiH+, based on the James-Coolidge method. The inner-electron orbitals are described by Slater-type atomic orbitals centered on Li, while the outer orbitals are described by elliptical orbitals of the type:

$$\eta^{l}\xi^{j}e^{-\alpha\xi}e^{im\phi} \qquad \text{(equation 1)}$$

where l and j are integers, and α is a nonlinear parameter, whose value was fixed at 1.35 in his paper, and optimized at 1.374 in an improved[78] calculation. It must be noted that these outer orbitals differ from what are generally recognized as elliptical orbitals[79] by the absence of an exponential in η. This gives the orbital an even or odd parity with respect the internuclear axis, but makes it difficult for these orbitals to correctly approximate two different atomic orbitals at large internuclear distances. Although not reported by Knipp, who published only binding energies, his 13-term wavefunction seemed to give an energy of -7.9848 hartree according to Ormand and Matsen, or -7.9913 hartree according to

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[77] J. K. Knipp, J. Chem. Phys. 4 , 300, (1936)

[78] F. T. Ormand and F. A. Matsen, J. Chem. Phys. 29 , 100 (1958)

[79] F. E. Harris, J. Chem. Phys. 32 , 3 (1959)

Ebbing.[80]

The use of mixed orbital sets, containing both atomic and elliptical orbitals, was later investigated by Browne and Matsen[81] who used elliptical functions of the type

$$\xi^{j}\eta^{l}[(\xi^{2}-1)(1-\eta^{2})]^{|m|/2}e^{-\alpha\xi}e^{-\gamma\eta}e^{im\phi}$$

(equation 2)

where α and γ are independently optimized nonlinear parameters. When the atomic orbitals were approximated by using a single optimized elliptical orbital, the energy obtained from this approximation turned out to be slightly lower than with the original orbitals.

The power and flexibility of elliptical functions was demonstrated by Harris and Taylor[82] who used a 3-term wavefunction of elliptical functions on the Li atom (thereby approximating an atomic wavefunction using functions more appropriate for diatomics) to obtain an energy of -7.4574 hartree (54% of the correlation energy). Their 4-term calculation for the LiH molecule gives an energy of -8.0387 hartree (62% of the correlation energy) at an internuclear distance of 3.2 atomic units. In both the atomic and the

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[80] D. D. Ebbing, J. Chem. Phys. 36, 1361 (1962)

[81] J. C. Browne and F. A. Matsen, Phys. Rev. 135, A1227 (1964)

[82] F. E. Harris and H. S. Taylor, Physica 30, 105 (1964)

molecular calculations, angular dependence was given to the wavefunction by including orbitals of the type:

$$\xi^{j}\eta^{l}[(\xi^{2}-1)(1-\eta^{2})]^{|m|/2}e^{-\alpha\xi}e^{-\beta\eta}e^{im\phi}$$

(equation 3)

with nonzero values of m. The allowed values of m are restricted by the symmetry of the state. Two configurations were sufficient to give an energy of -8.0138 hartree, compared with the Hartree-Fock energy[83] of -7.9873 hartree. Progressively more accurate calculations have been published using elliptical functions for lithium hydride. Table III shows some of the results obtained by Ebbing[84], Brown and Shull[85], Brown[86], and Bishop and Cheung[87], most notably. The flexibility of these elliptical-orbital calculations makes them particularly useful to such applications as the calculation of higher electronic states, where most of the same orbitals and configurations can be re-used, or are at least quite similar, and to potential

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[83] P.E. Cade and W. Huo, J. Chem. Phys. <u>47</u>, 614 (1967)

[84] D.D. Ebbing, J. Chem. Phys. <u>36</u>, 1361 (1962)

[85] R.E. Brown and H. Shull, Int. J. Q. Chem. <u>2</u>, 663 (1968)

[86] R.E. Brown, Ph.D. Thesis, Indiana University, 1967

[87] D.M. Bishop and L.M. Cheung, J. Chem. Phys. <u>78</u>, 1396 (1983)

energy curves, where, at least in the vicinity of the internuclear distance for which the orbitals were optimized, nonlinear parameters can simply be scaled for each internuclear distance. When these elliptical orbitals are transformed among themselves to produce natural orbitals, such as was done by Bender and Davidson[88], the results are even more striking. Their lowest ground-state energy for a 45-configuration wavefunction using 23 natural orbitals obtained from 32 elliptical orbitals was -8.0606 hartree (89% of the correlation energy). These results for elliptical functions compare very favorably with the large CI calculations performed by Ornellas and Hagstrom,[89] Langhoff and Chong[90], and even the very large CI calculation performed by Handy et al.[91] This calculation consisted of all single and double excitations from a $1\sigma 2\sigma 3\sigma 4\sigma 1\pi$ active space into 162 other orbitals.

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[88] C.F. Bender and E.R. Davidson, J. Phys. Chem. 70, 2675 (1966)

[89] F.R. Ornellas and S. Hagstrom, Theoret. Chim. Acta 62, 87 (1982)

[90] S.R. Langhoff and D.P. Chong, J. Chem. Phys. 69, 194 (1978)

[91] N.C. Handy, R.J. Harrison, P.J. Knowles, H.F. Schaefer III, J. Phys. Chem. 88, 4852 (1984)

TABLE III

LiH variational wavefunctions

ref.	no. of terms	type of terms	energy (% corr.)	dipole moment	R
77	13	atomic and elliptic	-7.9848 or -7.9913		3.00
78	10	atomic and elliptic	-7.9799	-5.574	3.00
81	28	atomic and elliptic	-8.0561	-5.93	3.046
81	24	elliptic	-8.0565 (65%)	-5.92	3.046
82	4	elliptic	-8.0387 (62%)		3.2
84	53	elliptic	-8.04128 (65%)	-5.96	2.99
85	69	elliptic	-8.0556 (83%)	-5.89	3.060
88	45	NO's from elliptic	-8.0606 (89%)	-5.9650	3.0147
87	411	elliptic 2 spin	-8.06553 (94.6%)	-5.8085	3.00
83	119	James-Coolidge	-8.0630 (91%)	-6.078	3.015
89	1852	Slater-type	-8.06347 (92%)		3.015
90	6514	CI	-8.0640 (93%)		
91	132015	CI	-8.06904 (98.4%)	-5.86	3.015

The flexibility of the representation of the correlating configurations may be a matter of some controversy. Clary[54] believes that correlating terms should ideally be the products of SCF or near-Hartree-Fock orbitals and powers of the interelectronic distances, while other authors favor using different[93] and usually simpler[94] basis sets for correlation. Using natural spin orbitals (NSO) or Brueckner (best overlap) orbitals would probably be a better route to a compact and accurate wavefunction, since these orbitals better describe[95] the electronic density of a correlated wavefunction. These orbitals are generally similar to SCF orbitals[96], but can usually[97] only be generated from a good correlated wavefunction. It is appealing to write a molecular wavefunction as a product of an uncorrelated function and some function of the interelectronic distances, and several authors[98] have used such wavefunctions,

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[93] H. James and A.S. Coolidge, J. Chem. Phys. 1, 825 (1933)

[94] K.M. Karunakaram and R.E. Christoffersen, Int. J. Quantum Chem. 22, 11 (1982)

[95] R.E. Brown and S. Larsson, Int. J. Quantum Chem., 12 83 (1977)

[96] S. Larsson and V.H. Smith, Jr., Phys. Rev. 178, 137 (1969)

[97] S. Larsson, J. Chem. Phys. 58, 5049 (1973)

[98] F. Berencz, Acta Phys. Acad. Sci. Hung. 6, 149 (1957)

usually for two-electron systems. The correlating functions can be constrained so that the wavefunction obeys Kato's equation[68] (equation 4 chapter 2) for the interelectronic cusp over all space, but only at the expense of the energy. In theory, the wavefunction could be expressed as a product of correlated and uncorrelated functions if the Schroedinger equation could be separated into such parts. This can only be done if the cross terms in the Laplacian are zero, which is not generally the case.

At the Hartree-Fock level, the best available calculations for many diatomics[99] are those that use a flexible basis set to describe each orbital by a function of the form

$$\psi_n^m(\xi\eta\Phi) = \sum_{l=|m|}^{L_n} X_{nl}^m(\xi)\, Y_l^m(\eta\Phi)$$

(equation 4)

similar to the James-Coolidge uncorrelated functions, where the $Y_l^m(\eta,\Phi)$ functions are spherical harmonics, and the $X_{nl}^m(\xi)$

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and 6,423 (1957) quoted by A.D. McLean, A. Weiss, and M. Yoshimine, Rev. Mod. Phys. 32, 205 (1960) ; M. Aubert-Frecon and C. LeSech, J. Chem. Phys. 74, 2931 (1981); C. LeSech et al., J. Chem. Phys. 75, 2932 (1981); J.W. Moscowitz and M.H. Kalos, Int. J. Quantum Chem. 20, 1107 (1981); S.F. Boys and N.C. Handy, Proc. Roy. Soc. A 309, 209 (1969); 310, 43 (1969); 310, 63 (1969); 311, 309 (1969)

[99] E.A. McCullough, Jr., J. Chem. Phys. 62, 3991, (1975)

functions are numerical functions to be determined by an iterative procedure.

In general, McCullough reports that the $X_{nl}^{m}(\xi)$ functions are very different from each other, even for orbitals of the same symmetry. In the Hartree-Fock treatment, the values of m are dictated by the symmetry of the state, and the upper limit on the sum over values of l depends on the rapidity of the convergence of the appropriate one-electron eigenvalues. It was found that the upper limit to the values of l necessary for good convergence were higher for the "inner" orbitals. This is understandable if the Hartree-Fock orbitals being approached are similar to elliptical functions. The same reasoning can be used for a basis set that does not have an exponential parameter in η.

A function made up of linear combinations of configurations of the type

$$\prod_{i=1}^{4} P_{l_i}(\eta_i)\,\xi_i^{j_i}\,e^{-\gamma_i \xi_i} \qquad \gamma_1 = \gamma_2 \,:\, \gamma_3 = \gamma_4 \qquad \text{(equation 5)}$$

will be a good approximation to one made up of functions of the type

$$\prod_{i=1}^{4} e^{-\beta_i \eta_i} e^{-\alpha_i \xi_i} \eta_i^{k_i} \xi_i^{j_i}$$

(equation 6)

provided that the ranges of the l_i included in the expansion be sufficient for the approximate relation

$$e^{-\beta_i \eta_i} = \sum_{k=1}^{N} a_{l,i} P_l(\eta_i)$$

(equation 7)

to hold within the required tolerance, and that the ranges of the k's be sufficient for the approximation

$$e^{-(\alpha_i - \gamma_i)\xi_i} = \sum_{k=1}^{M} a_{k,i} \xi_i^{k_i}$$

(equation 8)

to also hold. This type of expansion reduces the need for a large number of nonlinear parameters or their extensive optimization.

In the first case, it is a simple matter to expand an exponential function in terms of orthogonal polynomials of the same variable. The expansion coefficients can be calculated simply as the integral

$$a_{l,j} = \int_{-1}^{1} e^{-\beta_i \eta_i} P_l(\eta_i)\, d\eta_i$$

(equation 9)

Since this is an expansion in terms of orthogonal polynomials, the values of the coefficients do not depend on the order of the expansion. For the second case, it is simply a matter of using the Taylor expansion

$$e^{(\alpha_i-\tau_i)\xi_i} = a_0+a_1\xi_i+a_2\xi_i^2+a_3\xi_i^3+\ldots \quad \text{(equation 10)}$$

For small enough exponential coefficients, the Taylor series will converge quite quickly.

The best one- and two-term elliptical wavefunctions of the type of equation 2 are those of Harris and Taylor, as mentioned earlier. Leaving aside, for now, the expansion in ξ necessary to reduce the number of nonlinear parameters to two, we can expand the products of the exponentials in η in terms of products of four Legendre polynomials to obtain a long expansion. By choosing only the terms of the expansion whose coefficients are within a factor of 0.00005 of the leading term, the first configuration can be represented with about 130 such functions, and the first two together with between 200 and 250 functions. If we wish to express a wavefunction of three nonlinear parameters in ξ using only two such parameters, the Taylor series expansion above must be used, multiplying the number of terms in the expansion by four or so. The number of additional terms will of course depend on the accuracy required and on the value of $(\alpha-\tau)$. The purpose of this third parameter would be, in part, to recover some of the "in-out" correlation, but since the correlation is provided explicitly, one can expect the simulated extra nonlinear parameter to have less importance, and many of the configurations of the full expansion will be found not to contribute to the electronic energy.

Since the optimal nonlinear parameters of a basis of elliptical molecular orbitals depend almost linearly on the internuclear distance, the expansion in ξ will converge more quickly for small internuclear distances. One can therefore expect that variationally optimized internuclear distances will be too short when the basis set in use has insufficient flexibility in the coordinate ξ. One can also suggest, although it was not done in this work, that the nonlinear parameters be optimized at a small internuclear distance using a small basis, and then be linearly extrapolated for larger distances.

Since atomic orbitals can be written in terms of elliptical functions, using simple relations like

$$e^{-kr_A} = e^{-k(R/2)(\xi-\eta)}$$

(equation 11)

where R is the internuclear distance and r_A is the distance from nucleus A, they can also be expanded in this basis set. Here again the speed of convergence of the expansion will depend on the size of the nonlinear parameters. This means that describing the atomic character of the inner shells will require a large expansion in η, while representing atomic polarization functions will require relatively short expansions in ξ.

The wavefunction used in this work

The wavefunction described in detail in this section is one used for the ground state of LiH. The same discussion can be applied to any four-electron diatomic and can easily be extended to larger diatomics.

The space part of the wavefunction used in this work is made up of a linear combination of configurations;

$$\psi = \sum_{k} c_k \Phi_k$$

(equation 12)

where c are the coefficients chosen to minimize the total energy. Each configuration is an antisymmetrized product of orbitals, correlation functions, and a spin function:

$$\Phi'_k = \phi_1^k(1)\,\phi_2^k(2)\,\phi_3^k(3)\,\phi_4^k(4)\,r_{12}^{n_{12}^k}\,r_{13}^{n_{13}^k}\,r_{14}^{n_{14}^k}\,r_{23}^{n_{23}^k}\,r_{24}^{n_{24}^k}\,r_{34}^{n_{34}^k}$$

$$\Phi = A\,[\Phi'_k\;\chi^k]$$

(equation 13)

Each orbital Φ_a^k has the following form:

(equation 14)

$$\Phi_a^k(l_a^k, m_a^k, j_a^k, \alpha_a^k) = P_{l_a^k}^{|m_a^k|}(\eta_a)(\xi_a^2-1)^{|m_a^k|/2}\ \xi_a^{j_a^k}\ e^{-\alpha_a^k \xi_a}\ e^{i m_a^k \phi_a}$$

(equation 15)

where (ξ, η, ϕ) are the elliptical coordinates. $P_l^{|m|}(\eta)$ is the associated Legendre polynomial, defined as:

$$P_l^{|m|}(\eta) = \frac{(1-\eta^2)^{|m|/2}}{2^l l!}\left(\frac{d}{d\eta}\right)^{l+|m|}(1-\eta^2)^l$$

(equation 16)

The subscript "a" and the superscript "k" refer to coordinates of electron "a" and the configuration "k".

The following restrictions are imposed on the configurations:

1) There is at most one interelectronic coordinate term in a configuration (at most one of $n_{12}^k, n_{13}^k, \ldots$ is not zero).

2) n_{ij}^k can be nonzero only when $m_i = m_j = 0$

3) The parameters are within the limits

$$-3 \le m_a^k \le 3$$
$$|m_a^k| \le l_a^k \le 9$$
$$0 \le j_a^k \le 4$$
$$0 \le n_{ab}^k \le 4$$

(equation 17)

For most configurations, there will be two values of α:

$$\alpha_1^k = \alpha_2^k \ ; \ \alpha_3^k = \alpha_4^k$$

(equation 18)

For "split-valence-shell" configurations, however,

$$\alpha_3^k \ne \alpha_4^k$$

(equation 19)

The following two (unnormalized) spin functions:

$$\chi = (\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)$$
$$\chi' = 2(\beta\beta\alpha\alpha+\alpha\alpha\beta\beta) - (\alpha\beta+\beta\alpha)(\alpha\beta+\beta\alpha)$$

(equation 20)

together span the space of the eigenfunctions of S^2. These functions have the following properties:

$$P_{12}\chi = P_{34}\chi = -\chi$$
$$P_{12}\chi' = P_{34}\chi' = \chi'$$

(equation 21)

where P_{ij} is the two-particle permutation operator.

An element of the matrix representation of an operator $\hat{O}$

in the basis of the configurations may be written in Dirac notation as:

$$O^{ab}_{ij} = \langle \Phi'_i \chi^a | \hat{O} | A(\Phi'_j \chi^b) \rangle$$

(equation 22)

The four-particle antisymmetrizer A, may be expressed as:

$$A = (-P_{14} - P_{23} + (1-P_{13})(1-P_{24}))\ (1-P_{12})\ (1-P_{34})$$

(equation 23)

Depending on the spin function, the ket may be re-expressed as:

$$\text{for } \chi : |(-P_{14}-P_{23}+(1-P_{13})(1-P_{24}))[(\chi\ (1+P_{12})(1+P_{34})\Phi'_j]\rangle$$
$$\text{for } \chi' : |(-P_{14}-P_{23}+(1-P_{13})(1-P_{24}))[(\chi'(1-P_{12})(1-P_{34})\Phi'_j]\rangle$$

(equation 24)

The 18 possible spin integrals, coming from the combinations of two spin functions and six permutation operators, can easily be stored and looked up in a table. It is important to notice that a configuration which is symmetric in either electrons 1 & 2 or 3 & 4 before antisymmetrization can not have a second spin function χ'. Symmetry to inversion of those pairs of electrons can result in great simplification of the calculation.

The absence of an exponential factor in η, as discussed earlier, makes it more difficult for the wavefunction to accurately describe the dissociation of the molecular orbitals into atomic orbitals at large internuclear distances. On the other hand it avoids "atomic bias" at smaller internuclear distances. A large enough number of terms in the wavefunction should adequately represent the atomic character of the electronic distribution near the equilibrium internuclear distance. Avoiding the exponential factor reduces the number of nonlinear terms to be optimized, simplifies the multielectron integrals, and removes the necessity for quadruple precision integrations that were experienced by Clary and Handy, as well as possible linear dependence problems.

One possible deficiency of this form of the wavefunction is that it does not allow explicit coupled correlation terms of the form $r_{12} r_{13}$ or $r_{12} r_{34}$. Allowing terms of this type would add an order of magnitude to the difficulty and length of the calculation, as well as preventing it from being a general method for all diatomics having four or more electrons.

However, it has been found by most authors in the case of LiH as well as Be that most of the correlation is intra-shell, so that the linked coupled terms can be expected to be even less important than the inter-shell correlation. In addition, the James-Coolidge method also allows for some

configuration interaction, which can be expected to retrieve any missing coupled radial, left-right, and
some angular correlation.

In order to test the accuracy of the program, test runs were made to compare this method to a calculation by Clary[54] on the LiH molecule. The energy calculation for the single configuration

$$e^{-\alpha_1(\xi_1+\xi_2)} \; e^{\beta_1(\eta_1+\eta_2)} \; e^{-\alpha_2(\xi_3+\xi_4)} \; e^{\beta_2(\eta_3+\eta_4)}$$

(equation 25)

was approximated by internal expansion, in the evaluation of the matrix elements of

$$e^{(\beta_i+\beta_j)\eta} = \sum_{k=0}^{M} c_k P_k^0(\eta)$$

(equation 26)

with different values of M. The results are presented in the following table

TABLE IV

M	Energy
3	-7.418940
5	-7.906371
7	-7.931576
9	-7.931992
Clary	-7.9320

Previous work on correlated wavefunctions (chapter 1) has demonstrated that nonlinear parameters optimized for small basis sets will not necessarily be the optimal values for larger basis sets, especially when the larger basis set includes explicitly correlated functions. After several attempts to optimize nonlinear parameters using different sizes of basis sets, obtaining each time different sets of coefficients, we decided to use the values of Clary's first two parameters for LiH, 4.024 and 1.318. The energy of the wavefunction with three nonlinear parameters also became more and more insensitive to the value of the third parameter as the size of the basis set was increased. Adding basis functions with powers of ξ made it even more insensitive.

CHAPTER 4

METHOD OF CALCULATION

While the wavefunction discussed in the previous chapter dealt explicitly with the ground state of LiH, the method presented here is a general one for any diatomic, subject only to the first two restrictions on page 58 . These restrictions ensure that the integrals encountered in a larger system will be the same as those in a four-electron system. It applies to both homonuclear and heteronuclear diatomics.

Using atomic units throughout (see appendix), we can split the Hamiltonian operator into the potential and the kinetic operators:

$$H = T + V = -\frac{1}{2}\sum_i \nabla^2_i + V$$

(equation 1)

The potential operator in elliptical coordinates for a diatomic molecule AB having nucleus A at the position ($\xi=1$, $\eta=1$) and nucleus B at ($\xi=1$, $\eta=-1$) is, in atomic units,

$$V = -\sum_{i=1}^{N}[Q(a)(\frac{R}{2}(\xi_i-\eta_i))^{-1} + Q(b)(\frac{R}{2}(\xi_i+\eta_i))^{-1}] + \sum_{i<j} r_{ij}^{-1}$$

$$= -\frac{2}{R}\sum_{i=1}^{N}[(Q(a)+Q(b))\xi_i+(Q(a)-Q(b))\eta_i]/(\xi_i^2-\eta_i^2) + \sum_{i<j} r_{ij}^{-1}$$

(equation 2)

where Q(a) stands for the charge of nucleus A and Q(b) for the charge on nucleus B. R is the internuclear distance, N is the number of electrons, and r_{ij} is the Euclidian distance between electron i and electron j.

The Laplacian operator in elliptical coordinates is[100]

$$\nabla^2 = (4/R^2)(\xi^2-\eta^2)^{-1}(\frac{\partial}{\partial\xi}[(\xi^2-1)\frac{\partial}{\partial\xi}] + \frac{\partial}{\partial\eta}[(1-\eta^2)\frac{\partial}{\partial\eta}]$$

$$+ [(1-\eta^2)^{-1}(\xi^2-1)^{-1}]\frac{\partial^2}{\partial\phi^2})$$

(equation 3)

Applying the Laplacian to the one-electron orbital Φ defined as

$$\Phi_a^k(l_a^k, m_a^k, j_a^k, \alpha_a^k) = P_{l_a^k}^{|m_a^k|}(\eta_a)(\xi_a^2-1)^{|m_a^k|/2}\xi_a^{j_a^k}e^{-\alpha_a^k\xi_a}e^{im_a^k/a}$$

(equation 4)

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[100] L. Pauling and E. B. Wilson, Jr., "Introduction to Quantum Mechanics" , p. 444, McGraw-Hill, New York (1935)

in chapter 3 is a simple matter, since the variables are separable.

We find that

$$\partial^2\Phi_a^k/\partial\phi_a^2 = -{m_a^k}^2\Phi_a^k$$

(equation 5)

(note that in our notation Φ is an orbital and ϕ is a variable).

We will, for the sake of simplicity, drop the superscript "k" from now on. The previous equation therefore becomes:

$$\partial^2\Phi_a/\partial\phi_a^2 = -m_a^2\Phi_a$$

(equation 6)

The next term of the Laplacian gives

$$\frac{\partial}{\partial\eta_a}[(1-\eta_a^2)\frac{\partial}{\partial\eta_a}]P_{l_a}^{m_a}(\eta_a) = [(1-\eta_a^2)\frac{\partial}{\partial\eta_a}P_{l_a}^{m_a}(\eta_a)-2\eta_a\frac{\partial}{\partial\eta_a}P_{l_a}^{m_a}(\eta_a)]$$

(equation 7)

Since the associated Legendre polynomial is a solution of the equation

$$(1-\eta^2)(d^2/d\eta^2)P_l^m(\eta) - 2\eta(d/d\eta)P_l^m(\eta) + [l(l+1)-m^2(1-\eta^2)^{-1}]P_l^m(\eta) = 0$$

(equation 8)

we can combine this with the previous equation to get the result

$$\frac{\partial}{\partial\eta_a}[(1-\eta_a^2)\frac{\partial}{\partial\eta_a}]P_{l_a}^{m_a}(\eta_a) = [m_a^2(1-\eta_a^2)^{-1}-l_a(l_a+1)]P_{l_a}^{m_a}(\eta_a)$$

(equation 9)

The Laplacian of the orbital thus becomes:

$$\nabla^2\Phi_a = (4/R^2)(\xi_a^2-\eta_a^2)^{-1}(\frac{\partial}{\partial\xi_a}[(\xi_a^2-1)\frac{\partial}{\partial\xi_a}]-m_a^2(\xi_a^2-1)^{-1}-l_a(l_a+1))\Phi_a$$

(equation 10)

Let $\Xi(\xi)$ be the part of the orbital in the variable ξ:

$$\Xi_a(\xi_a) = (\xi_a^2-1)^{|m_a|/2}\xi_a^{j_a}e^{-\alpha_a\xi_a}$$

(equation 11)

Then,

$$\frac{\partial}{\partial\xi_a}[(\xi_a^2-1)\frac{\partial}{\partial\xi_a}]\Xi_a(\xi_a) = \frac{\partial}{\partial\xi_a}(\xi_a^2-1)[|m_a|(\xi_a^2-1)^{-1}\xi_a+j_a\xi_a^{-1}-\alpha_a]\Xi_a(\xi_a)$$

(equation 12)

$$= \frac{\partial}{\partial\xi_a}[|m_a|\xi_a+j_a(\xi_a-\xi_a^{-1})-\alpha_a(\xi_a^2-1)]\Xi_a(\xi_a)$$

(equation 13)

$$\begin{aligned} = \quad & -\alpha_a[|m_a|(\xi_a^2-1)^{-1}\xi_a^3 + (j_a+2)\xi_a - \alpha_a\xi_a^2] \\ & +(|m_a|+j_a)[|m_a|(\xi_a^2-1)^{-1}\xi_a^2 + (j_a+1) - \alpha_a\xi_a] \\ & +\alpha_a[|m_a|(\xi_a^2-1)^{-1}\xi_a + j_a\xi_a^{-1} - \alpha_a] \\ & -j_a[|m_a|(\xi_a^2-1)^{-1} + (j_a-1)\xi_a^{-2} - \alpha_a\xi_a^{-1}]\,\Xi_a(\xi_a) \end{aligned}$$

(equation 14)

$$= -2\alpha_a(j_a+|m_a|+1)\xi_a + (j_a+|m_a|+1)(j_a+|m_a|) + m_a^2(\xi_a^2-1)^{-1} + \alpha_a^2(\xi_a^2-1)$$
$$+ 2\alpha_a j_a \xi_a^{-1} - j_a(j_a-1)\xi_a^{-2} \quad \Xi_a(\xi_a)$$

(equation 15)

The Laplacian of the one-electron orbital can therefore be expressed as:

$$\nabla^2\Phi_a = (-2\alpha_a(j_a+|m_a|+1)\xi_a + (j_a+|m_a|+1)(j_a+|m_a|) + \alpha_a^2(\xi_a^2-1)$$
$$+ 2\alpha_a j_a \xi_a^{-1} - j_a(j_a-1)\xi_a^{-2} - l_a(l_a+1)) \quad \Phi_a(\xi_a)$$

(equation 16)

When the wavefunction contains a power of an interelectronic distance, the coordinates are not so easily separated. The Laplacian with respect to the coordinates of electron "a" of a product of a one-electron orbital and a power of an interelectronic distance would be:

$$\frac{\nabla_a^2[\Phi_a\Phi_b r_{ab}^{n_{ab}}]}{\Phi_a\Phi_b r_{ab}^{n_{ab}}} = \frac{\nabla_a^2\Phi_a}{\Phi_a} + \frac{\nabla_a^2 r_{ab}^{n_{ab}}}{r_{ab}^{n_{ab}}} + 2\frac{\nabla\Phi_a}{\Phi_a}\frac{\nabla r_{ab}^{n_{ab}}}{r_{ab}^{n_{ab}}}$$

(equation 17)

The first term on the right of the equation has already been derived. The second term, according to James and Coolidge[44], reduces to

$$\frac{\nabla^2 r_{ab}^{n_{ab}}}{r_{ab}^{n_{ab}}} = r_{ab}^{-(n_{ab}+2)} [2r_{ab}\frac{\partial}{\partial r_{ab}}(r_{ab}^{n_{ab}}) + r_{ab}^2\frac{\partial^2}{\partial r_{ab}^2}(r_{ab}^{n_{ab}})]$$

$$= r_{ab}^{-(n_{ab}+2)} [2n_{ab} + n_{ab}(n_{ab}-1)] r_{ab}^{n_{ab}}$$

$$= n_{ab}(n_{ab}+1) r_{ab}^{-2}$$

(equation 18)

and the third term can be re-expressed using[82]

$$\nabla\Phi_a \nabla r_{ab}^{n_{ab}} = (4/R^2)(\xi_a^2-\eta_a^2)^{-1} (\xi_a^2-1)\frac{\partial\Phi_a}{\partial\xi_a}\frac{\partial r_{ab}^{n_{ab}}}{\partial\xi_a} + (1-\xi_a^2)\frac{\partial\Phi_a}{\partial\xi_a}\frac{\partial r_{ab}^{n_{ab}}}{\partial\xi_a}$$

$$+ [\frac{1}{(1-\eta_a^2)} + \frac{1}{(\xi_a^2-1)}] \frac{\partial\Phi_a}{\partial\Phi_a}\frac{\partial r_{ab}^{n_{ab}}}{\partial\Phi_a}$$

(equation 19)

Because of restriction 2 on the wavefunction, (page 58) stating that the power of any interelectronic distance will be zero when one of the corresponding one-electron orbitals has a dependence on ϕ, this reduces to

$$\frac{\nabla\Phi_a \nabla r_{ab}^{n_{ab}}}{\Phi_a r_{ab}^{n_{ab}}} = (4/R^2)(\xi_a^2-\eta_a^2)^{-1} \frac{(\xi_a^2-1)}{\Phi_a r_{ab}^{n_{ab}}} \frac{\partial\Phi_a}{\partial\xi_a} \frac{\partial r_{ab}^{n_{ab}}}{\partial\xi_a}$$

$$+ \frac{(1-\eta_a^2)}{r_{ab}^{n_{ab}} P_{l_a}^0(\eta_a)} \frac{P_{l_a}^0(\eta_a)}{\eta_a} \frac{r_{ab}^{n_{ab}}}{\eta_a}$$

(equation 20)

According to James and Coolidge[44]

$$(\xi_a^2-1)(\partial r_{ab}^{n_{ab}}/\partial\xi_a) = \frac{n_{ab}}{2} r_{ab}^{n_{ab}-2} \xi_a r_{ab}^2 + \frac{R^2}{4}[\xi_a^3-\xi_a(\xi_b^2-\eta_a^2-\eta_b^2) + 2\eta_a\eta_b\xi_b]$$

(equation 21)

and it has been shown earlier that

$$\partial\Phi_a/\partial\xi_a = [|m_a|(\xi_a^2-1)^{-1}\xi_a + j_a\xi_a^{-1} - \alpha_a]\Phi_a$$

(equation 22)

or because of the restrictions on the values of m_a,

$$\partial\Phi_a/\partial\xi_a = [j_a\xi_a^{-1} - \alpha_a]\Phi_a$$

(equation 23)

Using the definition of the associated Legendre functions as the solutions to the differential equation

$$P_l^{|m|}(\eta) = \frac{(1-\eta^2)^{|m|/2}}{2^l l!}\left(\frac{d}{d\eta}\right)^{l+|m|}(1-\eta^2)^l$$

(equation 24)

one finds that

$$(d/d\eta_a)P_l^0(\eta_a) = (1-\eta_a^2)^{-1/2}\ P_l^1(\eta_a)$$

(equation 25)

when the value of l is not equal to zero. The derivative of $P_0^0(\eta)$ is 0.

In order to evaluate

$$(\partial r_{ab}^{n_{ab}}/\partial\eta_a) = n_{ab} r_a^{n_{ab}-1} (\partial r_{ab}/\partial\eta_a)$$

(equation 26)

we differentiate with respect to η_a the expansion

$$r_{ab}^2 = (R^2/4)\ \xi_a^2 + \xi_b^2 + \eta_a^2 + \eta^2{}_b - 2 - 2\xi_a\xi_b\eta_a\eta_b$$
$$- [(\xi_a^2-1)(\xi_b^2-1)(1-\eta_a^2)(1-\eta_b^2)]^{1/2}(e^{i(\phi_a-\phi_b)} + e^{i(\phi_b-\phi_a)})$$

(equation 27)

and obtain:

$$\partial r_{ab}/\partial\eta_a = r_{ab}^{-1}(R^2/4)\ \xi_a - \xi_a\xi_b\eta_a$$
$$+ \frac{1}{2}\eta_a(1-\eta_a^2)^{-1/2}[(\xi_a^2-1)(\xi_b^2-1)(1-\eta_a^2)]^{1/2}(e^{i(\phi_a-\phi_b)} + e^{i(\phi_b-\phi_a)})$$

(equation 28)

One can now obtain the expression:

$$\frac{(1-\eta_a^2)}{r^{n_{ab}} P^0_{l_a}(\eta\ )} \; \frac{P^0_{l_a}(\eta_a)}{\eta_a} \frac{r_{ab}^{n_{ab}}}{\eta_a} = \frac{R^2}{2} n_{ab} r_{ab}^{-2} [P^1_{l_a}(\eta_a)/P^0_{l_a}(\eta_a)]$$

$$(1-\eta_a^2)^{1/2} (\eta_a - \xi_a \xi_b \eta_b) +$$

$$+ \frac{1}{2} \eta_a (1-\eta_a^2)^{-1/2} [(\xi_a^2-1)(\xi_b^2-1)(1-\eta_a^2)]^{1/2} (e^{i(\phi_a-\phi_b)} + e^{i(\phi_b-\phi_a)})$$

(equation 29)

Noting that

$$(1-\eta^2)^{1/2} P^1_l(\eta) = \frac{l(l+1)}{2l+1} [P^0_{l-1}(\eta) - P^0_{l+1}(\eta)]$$

(equation 30)

one finally obtains the expression:

$$\frac{\nabla\Phi_a \nabla r_{ab}^{n_{ab}}}{\Phi_a r_{ab}^{n_{ab}}} = \frac{1}{\xi_a^2-\eta_a^2} \; \frac{n_{ab}}{2} (j_a \xi_a^{-1} - \alpha_a) [\frac{4}{R^2} \xi_a + r_{ab}^{-2} (\xi_a^3 - \xi_a (\xi_b^2+\eta_a^2+\eta_b^2) + 2\eta_a \eta_b \xi_b)]$$

$$+ (n_{ab} r_{ab}^{-2}/P^0_{l_a}(\eta_a)) [\frac{l_a(l_a+1)}{2l_a+1} (P^0_{l_a-1}(\eta_a) - P^0_{l_a-1}(\eta_a)) (\eta_a - \xi_a \xi_b \eta_a)$$

$$+ \frac{1}{2} \eta_a (1-\eta_a^2)^{-1/2} [(\xi_a^2-1)(\xi_b^2-1)(1-\eta_a^2)]^{1/2} (e^{i(\phi_a-\phi_b)} + e^{i(\phi_b-\phi_a)}))$$

(equation 31)

In order to evaluate this expression in a computer program, we will also need to make use of the following equivalences:

$$\eta[P^0_{l-1}(\eta) - P^0_{l+1}(\eta)] = \frac{l-1}{2l-1}P^0_{l-2}(\eta) + [\frac{l}{2l-1} - \frac{l+1}{2l+3}]P^0_l(\eta) - \frac{l+2}{2l+3}P^0_{l+2}(\eta)$$

(equation 32)

and

$$\eta P^1_l(\eta) = \frac{l+1}{2l+1}P^1_{l-1}(\eta) + \frac{l}{2l+1}P^1_{l+1}(\eta)$$

(equation 33)

Expansion of the matrix elements

We will need, in order to calculate values such as the energy, multipole moments, and other expectation values from variational as well as other wavefunctions, the seven matrix representations of five even and two odd operators, defined as follows:

$$S^e_{jk} = \int \Phi^*_j \Phi_k d\tau$$

(equation 34)

$$V^e_{jk} = \int \Phi^*_j [\sum_i ((Q(a)+Q(b))\xi_i/(\xi_i^2-\eta_i^2)) + \sum_{h<i} r^{-1}_{hi}]\Phi_k d\tau$$

(equation 35)

$$T^e_{jk} = \int \Phi^*_j \sum_i \nabla^2_i \Phi_k d\tau$$

(equation 36)

$$Q^{e}_{jk} = \int \Phi^{*}_{j} \sum_{i} (\xi_{i}^{2}\eta_{i}^{2}) \Phi_{k} d\tau$$

(equation 37)

$$R^{e}_{jk} = \int \Phi^{*}_{j} \sum_{i} (\xi_{i}^{2}+\eta_{i}^{2}) \Phi_{k} d\tau$$

(equation 38)

$$V^{o}_{jk} = \int \Phi^{*}_{j} \sum_{i} ((Q(a)-Q(b))\eta_{i}/(\xi_{i}^{2}-\eta_{i}^{2}))\Phi_{k} d\tau$$

(equation 39)

$$D^{o}_{jk} = \int \Phi^{*}_{j} \sum_{i} (\xi_{i}\eta_{i}) \Phi_{k} d\tau$$

(equation 40)

The superscript e and o denote even and odd matrices, respectively; an even operator has nonzero matrix elements between configurations of the same parity only, while odd operators have nonzero elements between those of different parity only. The sums are over all electrons or pairs of electrons, the integration is over all coordinates, and the volume element $d\tau$ is

$$d\tau = \mathop{\pi}\limits_{a=1}^{N} (R/2)^{3}(\xi_{a}^{2}-\eta_{a}^{2})\, d\xi_{a}\, d\eta_{a}\, d\phi_{a}$$

(equation 41)

In order that the integrals can be evaluated, the two configurations, the volume element, the conjugate complex, the $r_{ij}{}^{2}$ expansions, as well as the different terms arising from the operators must be reduced to a linear combination of seven basic integral types. A number of equivalences need to be used in this process. The principal ones are:[100]

$$(2l+1)(1-\eta^2)^{1/2}(\xi^2-1)^{1/2}e^{i\phi}\Phi(l,m,j,\alpha)=\Phi(l+1,m+1,j,\alpha)-\Phi(l-1,m+1,j,\alpha)$$

(equation 42)

$$\frac{2l+1}{l(l+1)}(1-\eta^2)^{1/2}(\xi^2-1)^{1/2}e^{-i\phi}\Phi(l,1,j,\alpha)=\Phi(l+1,0,j,\alpha)-\Phi(l-1,0,j,\alpha)$$

(equation 43)

$$(2l+1)\eta\Phi(l,1,j,\alpha)=(l+m)\Phi(l-1,m,j,\alpha)-(l-m+1)\Phi(l+1,m,j,\alpha)$$

(equation 44)

$$\eta^2\Phi(l,m,j;\alpha) = \frac{(l+m)(l+m-1)}{(2l+1)(2l-1)}\Phi(l-2,m,j,\alpha) + \frac{2l(l+1)-1-2m^2}{(2l-1)(2l+3)}\Phi(l,m,j,\alpha) + \frac{(l-m+1)(l-m+2)}{(2l+1)(2l+3)}\Phi(l+2,m,j,\alpha)$$

(equation 45)

$$\xi^k\Phi(l,m,j,\alpha) = \Phi(l,m,j+k,\alpha)$$

(equation 46)

$$P_l^{-m}(\eta) = \frac{(l-m)!}{(l+m)!}P_l^m(\eta)$$

(equation 47)

Using these equivalences or combinations of them, as well as the expansion of $r_{ij}^{\ 2}$ seen on page 71, all matrix elements can be reduced to linear combinations of integrals of the form

$$\underbrace{\int\int\int\cdots\int}_{3N} R \prod_{a=1}^{N} [\Phi_a(l_a, m_a, j_a, \alpha_a) \; \Phi'_a(l'_a, m'_a, j'_a, \alpha'_a)\, d\xi_a d\eta_a d\phi_a]$$

of them

(equation 48)

The Φ does not represent an orbital, but a one-electron function of the same form.

Seven different types of integral are produced, corresponding to the seven forms of R:

I: $R = 1$
II: $R = r_{ab}^{-1}$
III: $R = r_{ab}^{-1} \; r_{cd}^{-1}$
IV: $R = r_{ab}^{-1} \; r_{ac}^{-1}$
V: $R = r_{ab}^{-1} \; r_{ac}^{-1} \; r_{ad}^{-1}$
VI: $R = r_{ab}^{-1} \; r_{bc}^{-1} \; r_{cd}^{-1}$
VII: $R = r_{ab}^{-1} \; r_{ac}^{-1} \; r_{bc}^{-1}$

(equation 49)

It is to be noted that the integral of type III is the product of two independent two-electron integrals of the type found in integral II.

The variables may be separated using the Neumann[102]

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[102] K. Rüdenberg, J. Chem. Phys. 19 1459 (1951); F. E. Neumann, "Vorselungen ueber die Theorie des Potentials und der Kugelfunktionen", B. G. Teubner, Leipzig, 1878, chapter 13; F. E. Neumann, Crelles Journal fuer reine und angew. Mathematik 37, 21 (1848)

expansion:

$$r_{ab}^{-1} = \frac{2}{R} \sum_{l_{ab}=0}^{\infty} \sum_{m_{ab}} (-1)^{m_{ab}} (2l_{ab}+1) \frac{(l_{ab}-|m_{ab}|)!}{(l_{ab}+|m_{ab}|)!}$$

$$Q_{l_{ab}}^{|m_{ab}|}(\xi_a) P_{l_{ab}}^{m_{ab}}(\eta_a) e^{im_{ab}\phi_a} P_{l_{ab}}^{|m_{ab}|}(\xi_b) P_{l_{ab}}^{-m_{ab}}(\eta_b) e^{-im_{ab}\phi_b} \; ; \; \xi_a > \xi_b$$

(equation 50)

In this expansion, one notes the presence of associated Legendre functions in two different variables, namely η, defined over the range $(-1,1)$, and ξ, defined over $(1,\infty)$. For this second one, the associated Legendre function of the first kind is defined by

$$P_l^{|m|}(x) = \frac{(x^2-1)^{|m|/2}}{2^l l!} \left(\frac{d}{dx}\right)^{l+|m|} (x^2-1)^l$$

(equation 51)

Since the Neumann expansion is over the half-space $(\xi_a > \xi_b)$, integrals in ξ must be split into two parts. In some of the integrals involving coordinates of four electrons, the space must be split into up to 24 parts for integration.

Integration over the variables η leads to trivial Kronecker delta expressions.[103] Integrals in η are

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[103] J. F. Brown, M. Sc. Thesis, Indiana University, 1978. These integrals are found in the appendix. The signs of m_{11}

performed analytically using the orthogonality property of the associated Legendre functions:

$$\int_{-1}^{1} P_l^{m}(x)\, P_n^{-m}(x)\, dx = \delta(l, n)\frac{2}{2l+1}$$

(equation 52)

and the Clebsch-Gordan Coefficients (as defined by Harris and Michels[104]),

$$P_l^{m}(x)\, P_{l'}^{m'}(x) = \sum_j C_{j,l,l'}^{m,m'}\, P_j^{m+m'}(x)$$

(equation 53)

Integrations in η are consolidated into more compact expressions after expanding the Neumann expansion and are integrated by numerical quadrature, to be discussed in chapter 5.

Integrations in η

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in case 'A' must be corrected

[104] F. Harris and H. Michels, Advances in Chemical Physics, I. Prigogine ed., 13, 205, Interscience, New York, 1967

Besides the trivial integrations mentioned earlier:

$$\int_{-1}^{1} P_{l_a}^{|m_a|}(\eta_a)\, P_{l'_a}^{|m'_a|}(\eta_a)\, d\eta_a$$

(equation 54)

which we will abbreviate as

$$\int_{-1}^{1} P_{l}^{|m|}(\eta)\, P_{l'}^{|m'|}(\eta)\, d\eta$$

(equation 55)

there are three types of integrals which occur in the calculation. These are integral 1:

$$\int_{-1}^{1} P_{l}^{|m|}(\eta)\, P_{l'}^{|m'|}(\eta)\, P_{l_{ab}}^{|m_{ab}|}(\eta)\, d\eta$$

(equation 56)

which is required for the integrals II, III, IV, V, and VI; integral 2:

$$\int_{-1}^{1} P_{l}^{|m|}(\eta)\, P_{l'}^{|m'|}(\eta)\, P_{l_{ab}}^{|m_{ab}|}(\eta)\, P_{l_{ac}}^{|m_{ac}|}(\eta)\, d\eta \quad ; \quad m+m' = 0$$

(equation 57)

which is required for the integrals IV, VI, and VII; and integral 3:

$$\int_{-1}^{1} P_{l}^{|m|}(\eta)\, P_{l'}^{|m'|}(\eta)\, P_{l_{ab}}^{|m_{ab}|}(\eta)\, P_{l_{ac}}^{|m_{ac}|}(\eta)\, P_{l_{ad}}^{|m_{ad}|}(\eta)\, d\eta \quad ; \quad m+m' = 0$$

(equation 58)

which is needed for integral V. The restrictions on the m's come from the integration in ϕ, and the form of the Neumann expansion.

Integral 1

In this as well as all the other integrals in η, the fact that $P_0^0(\eta) = 1$ reduces the integral to a simpler one if any of (l, l', l_{ab}) is zero.

Of (m, m', m_{ab}), the one with the largest absolute value is called M, the one with the smallest absolute value is called M_a, and the other is called M_b. The corresponding l's are named L, L_a, and L_b.

Now,

$$|M| = |M_a| + |M_b| = |M_a + M_b|$$
$$M = -(M_a + M_b)$$

(equation 59)

Using the Clebsch-Gordan coefficients to expand products of associated Legendre functions, the integral may be rewritten and evaluated as

$$I1 = \int_{-1}^{1} P_{L_a}^{M_a}(\eta)\, P_{L_b}^{M_b}(\eta)\, P_L^M(\eta)\, d\eta$$

(equation 60)

$$I1 = \int_{-1}^{1} \sum_{j} C^{M_a, M_b}_{j, L_a, L_b} P_L^{-M}(\eta) P_L^{M}(\eta)\, d\eta$$

(equation 61)

$$= C^{M_a, M_b}_{L, L_a, L_b} \frac{(L+M)!}{(L-M)!} \frac{2}{2L+1}$$

(equation 62)

restrictions on the values of the Clebsch-Gordan coefficients are such that the integral is zero unless

$$\max(|M_a + M_b| , |L_a + L_b|) \le L \le (L_a + L_b)$$

$L + L_a + L_b$ is even.

(equation 63)

The notation max(a, b) signifies the greater of the two values.

Integral 2

There exist two possible cases for this integral. In the first case, it is possible to assign the names (M_a, M_b, M_c, M_d) to the values of (m, m', m_{ab}, m_{ac}) such that

$$M_a + M_b = M_c + M_d = M$$

$$M_a \ge M_b \; ; \; M_c \ge M_d$$

(equation 64)

The integral can then be solved as

$$I2 = \int_{-1}^{1} \sum_j C^{M_a, M_b}_{j, L_a, L_b} P^M_j(\eta) \sum_k C^{M_c, M_d}_{k, L_c, L_d} P^M_k(\eta)\, d\eta$$

(equation 65)

$$= \sum_L C^{M_a, M_b}_{L, L_a, L_b} C^{M_c, M_c}_{L, L_c, L_d} \frac{(L+M)!}{(L-M)!} \frac{2}{2L+1}$$

(equation 66)

The integral will equal zero unless:

$$\max(|M|, |L_a-L_b|, |L_c-L_d|) \le L \le \min((L_a+L_b), (L_c+L_d))$$

(equation 67)

$(L_a+L_b+L_c+L_d)$ is even

(L_a+L_b+L) is even

(equation 68)

$$M = M_d \; ; \; M_a \ge M_b \; ; \; M_a+M_b \ge M_c$$

(equation 69)

In the second case, the names are assigned such that

$$M_a+M_b+M_c = M_d = M \; ; \; M_a \ge M_b \; ; \; M_a+M_b \ge M_c$$

(equation 70)

The integration is then:

$$I1 = \int_{-1}^{1} \sum_L C^{M_a, M_b}_{L, L_a, L_b} C^{M_a+M_b, M_c}_{L_d, L, L_c} P^M_L(\eta) P^M_L(\eta)\, d\eta$$

(equation 71)

$$= C^{M_a, M_b}_{L, L_a, L_b} C^{M_a+M_b, M_c}_{L_d, L, L_c} \frac{(L_d+M)!}{(L_d-M)!} \frac{2}{2L_d+1}$$

(equation 72)

Restrictions on the Clebsch-Gordan coefficients make the integral zero unless

$$\max(|M_a+M_b| , |L_a-L_b|) \leq L \leq (L_a+L_b)$$

(equation 73)

$$\max(|M| , |L_c-L|) \leq L_d \leq (L_c+L)$$

(equation 74)

$(L_a+L_b+L_c+L_d)$ is even

(L_a+L_b+L) is even

(equation 75)

Integral 3

Here again, there are two possibilities. The ratio of positive and negative m's may be 2:3 or 1:4.

In the first case,

$$M_a+M_b+M_c = M_d = M \; ; \; M_a \geq M_b \; ; \; M_a+M_b \geq M_c$$

(equation 76)

$$I3 = \int_{-1}^{1} \Big(\sum_{L} C^{M_a, M_b}_{L, L_a, L_b} \sum_{L'} C^{M_a+M_b, M_c}_{L', L, L_c} P^{M}_{L'}(\eta) \Big) \Big(\sum_{L''} C^{M_d, M_e}_{L'', L_d, L_e} P^{-M}_{L'}(\eta) \Big) d\eta$$

(equation 77)

$$I3 = \sum_{L} C^{M_a, M_b}_{L, L_a, L_b} \sum_{L'} C^{M_a+M_b, M_c}_{L', L, L_c} \; C^{M_d, M_e}_{L', L_d, L_e} \; \frac{2}{2L'+1}$$

(equation 78)

The integral equals zero unless

$\max((M_a+M_b) \; , \; (L_a-L_b) \le L \le (L_a+L_b)$.

$\max(M \; , \; (L-L_c) \; , \; (L_d-L_e) \le L' \le \min((L+L_c) \; ; \; (L_d+L_e))$

$L_a+L_b+L_c+L_d+L_e$ is even

L_a+L_b+L is even

L_d+L_e+L' is even

(equation 79)

In the second case,

$M_a+M_b+M_c+M_d = M_e = M \; ; \; M_a \ge M_b \; ; \; M_c \ge M_d \; ; \; M_a+M_b \ge M_c+M_d$

(equation 80)

the integral may be calculated as

$$I3 = \Big(\sum_{L} C^{M_a, M_b}_{L, L_a, L_b} \sum_{L'} C^{M_c, M_d}_{L', L_c, L_d} \; C^{M_a+M_b, M_c+M_d}_{L_e, L, L'} \Big) \; \frac{2}{2L_e+1}$$

(equation 81)

The integral equals zero unless

$$\max((M_a+M_b)\ ,\ (L_a-L_b)) \leq L \leq (L_a+L_b)$$

$$\max((M_c+M_d)\ ,\ (L_e-L)\ ,\ (L_c-L_d)) \leq L' \leq \min((L_e+L)\ ,\ (L_c+L_d))$$

$$(L-L') \leq L_e \leq (L+L')$$

$$L_a+L_b+L_c+L_d+L_e \text{ is even}$$

$$L_a+L_b+L \text{ is even}$$

$$L_d+L_e+L' \text{ is even}$$

(equation 82)

Integrations in ξ.

These are by far the most difficult integrals to evaluate. In most cases, this must be done by numerical quadrature. There are six types of integrals, involving one, two, three, or four electrons. Each will be dealt with separately. The integrals in the 3N coordinates of the N electrons linked by reciprocal interelectronic distances will be discussed in the following sections. Each defines a different integral in ξ.

The integral $\langle\ \rangle$

This integral contains no reciprocal internuclear distance. It is the simplest and most common integral encountered, involving the coordinates of one electron. It occurs in integrals of type I, II, and IV. It is of the form

$$\langle\rangle = \iiint \Phi_a(l_a, m_a, j_a, \alpha_a)\ \Phi'_a(l'_a, m'_a, j'_a, \alpha'_a)\, d\xi_a d\eta_a d\phi_a$$

(equation 83)

When the integrations in η and ϕ are carried out and replaced into this integral, we obtain:

$$\langle\rangle = 4\pi\ \delta(m_a, -m'_a)\ \delta(l_a, l'_a)\ 1/(2l_a+1)\ \int_1^\infty (\xi_a^2-1)^{|m_a|}\ \xi_a^{j_a+j'_a} e^{-(\alpha_a+\alpha'_a)\xi_a} d\xi_a$$

(equation 84)

Integrals of the form

$$\int_1^\infty \xi^j e^{-\alpha\xi} d\xi$$

(equation 85)

are easily evaluated and will be dealt with in a later section, page 114.

The integral $\langle r_{ab}^{-1}\rangle$

This particular integral has appeared in the literature a number of times. It occurs in integrals of type II or III, and involves the coordinates of two electrons, linked by a reciprocal interelectronic distance. Replacing the Neumann expansion into the integral, we obtain:

$$
\begin{aligned}
\langle r_{ab}^{-1} \rangle = {} & \frac{2}{R}(2\pi)^{2}(-1)^{m_{ab}} \sum_{l_{ab}=|m_{ab}|}^{\infty} (2l_{ab}+1)\left[\frac{(l_{ab}-|m_{ab}|)!}{(l_{ab}+|m_{ab}|)!}\right]^{2} \\
& \int_{-1}^{1} P_{l_a}^{m_a}(\eta_a) P_{l'_a}^{m'_a}(\eta_a)\, d\eta_a \int_{-1}^{1} P_{l_b}^{m_b}(\eta_b) P_{l'_b}^{m'_b}(\eta_b)\, d\eta_b \\
& \Big[\int_{1}^{\infty} e^{-(\alpha_a+\alpha'_a)\xi_a}\, \xi_a^{j_a+j'_a} (\xi_a^{2}-1)^{(|m_a|+|m'_a|)/2}\, Q_{l_{ab}}^{|m_{ab}|}(\xi_a) \\
& \cdot \int_{1}^{\xi_a} e^{-(\alpha_b+\alpha'_b)\xi_b}\, \xi_b^{j_b+j'_b} (\xi_b^{2}-1)^{(|m_b|+|m'_b|)/2}\, P_{l_{ab}}^{|m_{ab}|}(\xi_b)\, d\xi_b\, d\xi_a \\
& + \int_{1}^{\infty} e^{-(\alpha_b+\alpha'_b)\xi_b}\, \xi_b^{j_b+j'_b} (\xi_b^{2}-1)^{(|m_b|+|m'_b|)/2}\, Q_{l_{ab}}^{|m_{ab}|}(\xi_b) \\
& \cdot \int_{1}^{\xi_b} e^{-(\alpha_a+\alpha'_a)\xi_a}\, \xi_a^{j_a+j'_a} (\xi_a^{2}-1)^{(|m_a|+|m'_a|)/2}\, P_{l_{ab}}^{|m_{ab}|}(\xi_a)\, d\xi_a\, d\xi_b \Big] \\
& \delta(m_a+m'_a+m_b+m'_b\,,\ 0)\ ; \quad m_{ab} = m_a+m'_a
\end{aligned}
$$

(equation 86)

The integrals involving the coordinates η_a and η_b as well as the Kronecker delta expression arising from the integrations in ϕ_a and ϕ_b, have been seen earlier. These integrations place restrictions on the value of m_{ab} and the possible values of l_{ab}, eliminating the infinite summation over these values. Note that the whole integral is zero unless $l_a + l'_a + l_b + l'_b$ is even.

The integral involving the coordinates ξ_a and ξ_b between square brackets, designated as [], may be abbreviated as:

$$[\,] = \int_1^\infty h_a(x)\, Q_{ab}(x) \int_1^x h_b(y)\, P_{ab}(y)\, dy dx \; + \; \int_1^\infty h_b(x)\, Q_{ab}(x) \int_1^x h_a(y)\, P_{ab}(y)\, dy dx$$
(equation 87)

where

$$h_a(x) = e^{-(\alpha_a+\alpha'_a)x}\, x^{j_a} (x^2-1)^{|m_{ab}|/2 \,+\, m''_a}$$
(equation 88)

$$h_b(x) = e^{-(\alpha_b+\alpha'_b)x}\, x^{j_b} (x^2-1)^{|m_{ab}|/2 \,+\, m''_b}$$
(equation 89)

$$P_{ab}(x) = P_{l_{ab}}^{|m_{ab}|}(x)$$
(equation 90)

$$Q_{ab}(x) = Q_{l_{ab}}^{|m_{ab}|}(x)$$
(equation 91)

$$m''_a = (|m_a| + |m'_a| - |m_a+m'_a|)/2$$
(equation 92)

Let

$$K_{ab}(x) = \int_1^x P_{ab}(y)\, h_b(y)\, dy.$$
(equation 93)

Now,

$$\frac{d}{dx}[K_{ab}(x)K_{ba}(x)] = P_{ab}(x)h_b(x)\int_1^x P_{ab}(y)h_a(y)\,dy + P_{ab}(x)h_a(x)\int_1^x P_{ab}(y)h_b(y)\,dy$$

(equation 94)

Putting this into the expression for [], we obtain:

$$[\,] = \int_1^\infty (Q_{ab}(x)/P_{ab}(x))\; d[K_{ab}(x)K_{ba}(x)]$$

(equation 95)

Integrating by parts, and keeping in mind the fact that

$$\lim_{x\to 1} K_{ab}(x)Q_{ab}(x)/P_{ab}(x) = \lim_{x\to \infty} K_{ab}(x)Q_{ab}(x)/P_{ab}(x) = 0$$

(equation 96)

we get:

$$[\,] = -\int_1^\infty G_{ab}(x)K_{ab}(x)K_{ba}(x)\,dx$$

(equation 97)

where

$$G_{ab}(x) = \frac{d}{dx}\left[\frac{Q_{ab}(x)}{P_{ab}(x)}\right] = \frac{(-1)^{m_{ab}}(l_{ab}+|m_{ab}|)!}{(l_{ab}-|m_{ab}|)!(1-x^2)[P_{l_{ab}}^{|m_{ab}|}(x)]^2}$$

(equation 98)

Having obtained a simple expression for the integral, we will now change the order of integration for reasons which will become clear later on, giving an integral which is probably a little more difficult to evaluate. Defining

$$W_{ab}(x) = P_{ab}(x)\int_x^\infty G_{ab}(y)K_{ab}(y)dy$$

(equation 99)

the integral [] can be re-expressed as:

$$[] = \int_1^\infty h_a(x)[Q_{ab}(x)K_{ab}(x) + P_{ab}(x)H_{ab}(x)]dx$$

(equation 100)

where

$$H_{ab}(x) = \int_1^x Q_{ab}(y)h_a(y)dy$$

(equation 101)

Integrating by parts the integral in $W_{ab}(x)$, we obtain

$$W_{ab}(x) = P_{ab}(x)[-K_{ab}(x)Q_{ab}(x)/P_{ab}(x) - \int_x^\infty Q_{ab}(y)/P_{ab}(y)h_b(y)dy]$$

(equation 102)

$$-W_{ab}(x) = Q_{ab}(x)K_{ab}(x) + P_{ab}(x)H_{ab}(x)$$

(equation 103)

Replacing this into the expression of the integral [], we obtain the following expression

$$[] = -\int_1^\infty h_a(x)W_{ab}(x)dx$$

(equation 104)

The integral $\langle r_{ab}^{-1}r_{ac}^{-1}\rangle$

The expression for the entire integral in this and subsequent cases is too unwieldy to write in its entirety. It is easily derived by replacing the appropriate Neumann expansions into the integral of type IV described earlier.

The integration in the coordinates ϕ_i fixes the values of m_{ab} and m_{ac} to

$$\pm m_{ab} = m_b + m'_b$$
$$\pm m_{ac} = m_c + m'_c$$

with the proviso that the integral is zero unless:

$$m_a + m'_a + m_b + m'_b + m_c + m'_c = 0$$

(equation 105)

Since the Neumann expansion will be summed over all m , positive or negative, the sign of the fixed m_{ab} may be chosen arbitrarily.

The integrations in η consist of two integrals of type 1 in η_b and η_c, and one integral of type 2 in η_a, with the restrictions on the values of the "l"'s that these imply.

The integration in ξ_i can be split into 4 parts, as imposed by the two half-space Neumann expansions.

① $\int_1^\infty P_{ab}(x)\, P_{ac}(x)\, h_a(x)\, H_{ab}(x)\, H_{ac}(x)\, dx$

② $\int_1^\infty P_{ab}(x)\, Q_{ac}(x)\, h_a(x)\, H_{ab}(x)\, K_{ac}(x)\, dx$

③ $\int_1^\infty Q_{ab}(x)\, P_{ac}(x)\, h_a(x)\, K_{ab}(x)\, H_{ac}(x)\, dx$

④ $\int_1^\infty Q_{ab}(x)\, Q_{ac}(x)\, h_a(x)\, K_{ab}(x)\, K_{ac}(x)\, dx$

(equation 106)

One can use the definition of $W_{ac}(x)$ to add ① and ②:

① + ② = $- \int_1^\infty P_{ab}(x)\, h_a(x)\, H_{ab}(x)\, W_{ac}(x)\, dx$

(equation 107)

and the same can be done for ③ and ④:

③ + ④ = $- \int_1^\infty Q_{ab}(x)\, h_a(x)\, K_{ab}(x)\, W_{ac}(x)\, dx$

(equation 108)

and again to add these last two:

① + ② + ③ + ④ = $\int_1^\infty h_a(x)\, W_{ab}(x)\, W_{ac}(x)\, dx$

(equation 109)

The integral $\langle r_{ab}^{-1} r_{ac}^{-1} r_{ad}^{-1} \rangle$

This integral is evaluated in the same manner as the previous one, by substituting the appropriate Neumann expansions into the integral of type V described earlier.

The integration in the coordinates ϕ_i give the conditions:

$$\pm m_{ab} = m_b + m'_b$$
$$\pm m_{ac} = m_c + m'_c$$
$$\pm m_{ad} = m_d + m'_d$$
$$m_a + m'_a + m_b + m'_b + m_c + m'_c + m_d + m'_d = 0$$
(equation 110)

The integrations in ξ consist of three integrals of type 1 and one integral of type 3, with the appropriate restrictions on the values of the "l"'s.

The integration in ξ can be split into 8 parts:

① $\int_1^\infty P_{ab}(x) P_{ac}(x) P_{ad}(x) h_a(x) H_{ab}(x) H_{ac}(x) H_{ad}(x)\, dx$

② $\int_1^\infty P_{ab}(x) P_{ac}(x) Q_{ad}(x) h_a(x) H_{ab}(x) H_{ac}(x) K_{ad}(x)\, dx$

③ $\int_1^\infty Q_{ab}(x) P_{ac}(x) P_{ad}(x) h_a(x) K_{ab}(x) H_{ac}(x) H_{ad}(x)\, dx$

④ $\int_1^\infty Q_{ab}(x) P_{ac}(x) Q_{ad}(x) h_a(x) K_{ab}(x) H_{ac}(x) K_{ad}(x)\, dx$

⑤ $\int_1^\infty P_{ab}(x) Q_{ac}(x) P_{ad}(x) h_a(x) H_{ab}(x) K_{ac}(x) H_{ad}(x)\, dx$

⑥ $\int_1^\infty Q_{ab}(x) Q_{ac}(x) P_{ad}(x) h_a(x) K_{ab}(x) K_{ac}(x) H_{ad}(x)\, dx$

⑦ $\int_1^\infty P_{ab}(x) Q_{ac}(x) Q_{ad}(x) h_a(x) H_{ab}(x) K_{ac}(x) K_{ad}(x)\, dx$

⑧ $\int_1^\infty Q_{ab}(x) Q_{ac}(x) Q_{ad}(x) h_a(x) K_{ab}(x) K_{ac}(x) K_{ad}(x)\, dx$

(equation 111)

These can be consolidated in three steps:

① + ② = $-\int_1^\infty P_{ab}(x) P_{ac}(x) h_a(x) H_{ab}(x) H_{ac}(x) W_{ad}(x)\, dx$

③ + ④ = $-\int_1^\infty Q_{ab}(x) P_{ac}(x) h_a(x) K_{ab}(x) H_{ac}(x) W_{ad}(x)\, dx$

⑤ + ⑥ = $-\int_1^\infty Q_{ac}(x) P_{ad}(x) h_a(x) K_{ac}(x) H_{ad}(x) W_{ab}(x)\, dx$

⑦ + ⑧ = $-\int_1^\infty Q_{ac}(x) Q_{ad}(x) h_a(x) K_{ac}(x) K_{ad}(x) W_{ab}(x)\, dx$

(equation 112)

$$① + ② + ③ + ④ = \int_1^\infty P_{ac}(x)\, h_a(x)\, H_{ac}(x)\, W_{ab}(x)\, W_{ad}(x)\, dx$$

$$⑤ + ⑥ + ⑦ + ⑧ = \int_1^\infty Q_{ac}(x)\, h_a(x)\, K_{ac}(x)\, W_{ab}(x)\, W_{ad}(x)\, dx$$

(equation 113)

$$① + ② + ③ + ④ + ⑤ + ⑥ + ⑦ + ⑧ = - \int_1^\infty h_a(x)\, W_{ab}(x)\, W_{ac}(x)\, W_{ad}(x)\, dx$$

(equation 114)

The integral $\langle r_{ab}^{-1} r_{bc}^{-1} r_{cd}^{-1} \rangle$

This integral is a bit more difficult to evaluate than the previous ones, since there does not seem to be a way to avoid performing a triple numerical integration.

The integration in the coordinates ϕ_i gives the conditions:

$$\pm m_{ab} = m_a + m'_a$$
$$\pm m_{cd} = m_d + m'_d$$
$$\pm m_{bc} = m_a + m'_a + m_b + m'_b$$
$$m_a + m'_a + m_b + m'_b + m_c + m'_c + m_d + m'_d = 0$$

(equation 115)

The integrations in η consist of two integrals of type 1 and two integrals of type 2, with the appropriate restrictions on the values of the "l"'s.

The 8-part integrals in $\mathcal{E}$ can easily be regrouped into these two:

$$\begin{aligned}&\int_1^\infty [Q_{ab}(x)K_{ba}(x) + P_{ab}(x)H_{ba}(x)]P_{bc}(x)h_b(x)\\ &\cdot \int_x^\infty Q_{bc}(y)h_c(y)[Q_{cd}(y)K_{cd}(y) + P_{cd}(y)H_{cd}(y)]\,dydx\\ &+ \int_1^\infty [Q_{cd}(x)K_{cd}(x) + P_{cd}(x)H_{cd}(x)]P_{cd}(x)h_c(x)\\ &\cdot \int_x^\infty Q_{bc}(y)h_b(y)[Q_{ab}(y)K_{ba}(y) + P_{ab}(y)H_{ba}(y)]\,dydx\end{aligned} \qquad \text{(equation 116)}$$

These can be reduced to:

$$\begin{aligned}&\int_1^\infty W_{ba}(x)P_{bc}(x)h_b(x)\int_x^\infty Q_{bc}(y)h_c(y)W_{cd}(y)\,dydx\\ &+ \int_1^\infty W_{cd}(x)P_{bc}(x)h_c(x)\int_x^\infty Q_{bc}(y)h_b(y)W_{ba}(y)\,dydx\end{aligned} \qquad \text{(equation 117)}$$

More algebraic manipulation with this expression can make it more compact or more elegant, but not necessarily easier to evaluate. It is therefore left in its present form. It must be noted that the "W" functions in the "inside" integrals are already the result of a numerical integration. There is therefore a triple numerical integration to be dealt with. It is also the first time that an associated Legendre function of the second kind must be evaluated explicitly. It is possible to eliminate it, but not very useful to do so, since it is difficult to avoid evaluating them for the next integral.

The integral $\langle r_{ab}^{-1} r_{ac}^{-1} r_{bc}^{-1} \rangle$

This integral is the most difficult one to evaluate for several reasons. First, the integration in the coordinates ϕ do not, as in all the previous integrals, reduce the sums over the parameters m_{ab}, etc., to a single term. Second, the Clebsch-Gordan coefficients arising from the integrations in η do not determine an absolute upper limit on the parameters l_{ab}, etc., in the infinite summations. We must rely on decreasing values of the integrals with increasing values of these parameters to ensure that the sum converges quickly. Moreover, many different integrals of this type are required, since they usually arise as the result of the product of at least two expansions of the squares of interelectronic coordinates.

Integrations in ϕ_i give the conditions:

$$\pm m_{ab} = m_b + m'_b + m_{bc}$$
$$\pm m_{ac} = m_c + m'_c - m_{bc}$$
$$m_a + m'_a + m_b + m'_b + m_c + m'_c = 0$$

A summation over the possible values of m_{bc} is required.

The integrations in η consist of three integrals of type 2. There is no absolute upper limit on the values of l_{ab}, etc. It is therefore possible for l_{ab}, l_{ac}, l_{bc} to reach high values. Fortunately, the contributions to the total integral from those portions having high values of the "l"'s rapidly becomes negligible. The integrations in η also restrict the parities of these parameters. Thus, the integral is zero unless:

$$l_{ab} + l_{ac} + l_a + l'_a \text{ is even}$$
$$l_{ab} + l_{bc} + l_b + l'_b \text{ is even}$$
$$l_{ac} + l_{bc} + l_c + l'_c \text{ is even}$$
$$l_a + l'_a + l_b + l'_b + l_c + l'_c \text{ is even}$$

(equation 119)

The integral is thus:

$$\int_1^\infty P_{ab}(x)\, Q_{ac}(x)\, h_a(x) [\int_1^x P_{bc}(y)\, P_{ac}(y)\, h_c(y)] [\int_x^\infty Q_{ab}(y)\, Q_{bc}(y)\, h_b(y)\, dy]\, dx \; +$$

$$\int_1^\infty P_{bc}(x)\, Q_{ac}(x)\, h_c(x) [\int_1^x P_{ab}(y)\, P_{ac}(y)\, h_a(y)] [\int_x^\infty Q_{ab}(y)\, Q_{bc}(y)\, h_b(y)\, dy]\, dx \; +$$

$$\int_1^\infty P_{ac}(x)\, Q_{ab}(x)\, h_a(x) [\int_1^x P_{ab}(y)\, P_{bc}(y)\, h_b(y)] [\int_x^\infty Q_{ac}(y)\, Q_{bc}(y)\, h_c(y)\, dy]\, dx \; +$$

$$\int_1^\infty P_{bc}(x)\, Q_{ab}(x)\, h_b(x) [\int_1^x P_{ab}(y)\, P_{ac}(y)\, h_a(y)] [\int_x^\infty Q_{ac}(y)\, Q_{bc}(y)\, h_c(y)\, dy]\, dx \; +$$

$$\int_1^\infty P_{ab}(x)\, Q_{bc}(x)\, h_b(x) [\int_1^x P_{bc}(y)\, P_{ac}(y)\, h_c(y)] [\int_x^\infty Q_{ab}(y)\, Q_{ac}(y)\, h_a(y)\, dy]\, dx \; +$$

$$\int_1^\infty P_{ac}(x)\, Q_{bc}(x)\, h_c(x) [\int_1^x P_{ab}(y)\, P_{bc}(y)\, h_b(y)] [\int_x^\infty Q_{ab}(y)\, Q_{ac}(y)\, h_a(y)\, dy]\, dx \; +$$

(equation 120)

We will first work with the first two lines, keeping in mind the fact that the other lines are permutations of these first two with respect to the subscripts. The two lines are combined to give the expression:

$$\int_1^\infty Q_{ab}(x)\, Q_{bc}(x)\, h_b(x) \int_1^x Q_{ac}(y) / P_{ac}(y) \;\; d/dy\, (\vert K_a(y) \;\vert K_c(y))\, dydx$$

(equation 121)

where

$$\vert K_b(x) \; = \; \int_1^x P_{ab}(y)\, P_{bc}(y)\, h_b(y)\, dy$$

(equation 122)

$$= \sum_L C^{m_{ab}, m_{bc}}_{L; l_{ab}, l_{bc}} \int_1^x P_L^{m_{ab}+m_{bc}}(y)\, h_b(y)\, dy$$

(equation 123)

Switching the order of integration, we get:

$$\int_1^\infty Q_{ac}(x)/P_{ac}(x) \;\; d/dx \; (|K_a(x) \; |K_c(x)) \int_x^\infty Q_{ab}(y)\, Q_{bc}(y)\, h_b(y)\, dydx$$

$$= \int_1^\infty Q_{ac}(x)[h_a(x)P_{ab}(x) \; |K_c(x) + h_c(x)P_{bc}(x) \; |K_a(x)] \; |H_b(x)\, dx$$

(equation 124)

where

$$|H_b(x) = \int_x^\infty Q_{ab}(y)\, Q_{bc}(y)\, h_b(y)\, dy$$

(equation 125)

Adding the other two permutations, the complete integral will be:

$$= \int_1^\infty Q_{ac}(x)[h_a(x)P_{ab}(x) \; |K_c(x) + h_c(x)P_{bc}(x) \; |K_a(x)] \; |H_b(x)\, dx$$

$$+\int_1^\infty Q_{bc}(x)[h_b(x)P_{ab}(x) \; |K_c(x) + h_c(x)P_{ac}(x) \; |K_b(x)] \; |H_a(x)\, dx$$

$$+\int_1^\infty Q_{ab}(x)[h_a(x)P_{ac}(x) \; |K_b(x) + h_b(x)P_{bc}(x) \; |K_a(x)] \; |H_c(x)\, dx$$

(equation 126)

CHAPTER 5

NUMERICAL INTEGRATION

Romberg Quadrature

The principal method of integration used in the program is Romberg quadrature. This method is based on the application of Richardson's[105] extrapolation to a trapezoidal rule integration.[106]

Suppose that the value of an integral is I. A trapezoidal rule quadrature using mesh size h_i can be shown[107] to equal:

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[105] L. F. Richardson, Phil. Trans. Roy. Soc. Lon. A 120 307 (1909)

[106] R. W. Hornbeck, "Numerical Methods", p. 150, Quantum Publishers, New York 1975.

[107] A. Ralston, "A first course in Numerical Analysis", McGraw-Hill, New York, 1965

$$I_1 = I - C(h_1)^2 - D(h_1)^4 - E(h_1)^6 - \ldots$$

(equation 1)

where C, D, E, etc., are constants depending on the values of the derivatives of the function to be evaluated at the end points of the integration.[108]

Now, if we perform a similar quadrature using the smaller mesh size $h_2 = h_1/2$, we obtain:

$$I_2 = I - C(h_2)^2 - D(h_2)^4 - E(h_2)^6 - \ldots$$

(equation 2)

$$I_1 = I - 4C(h_2)^2 - 16D(h_2)^4 - 64E(h_2)^6 - \ldots$$

(equation 3)

The two approximate integrations can now be combined so as to eliminate the second order error term:

$$(4I_2 - I_1)/3 = I + 4D(h_2)^4 + 20E(h_2)^6 + \ldots$$

(equation 4)

A new approximate integral can be evaluated using a still smaller mesh size $h_3 = h_2/2 = h_1/4$. The approximate integral I_3 obtained from this step can similarly be combined with integral I_2 as before:

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[108] N. C. Handy, S. F. Boys, Theor. Chim. Acta, 31, 195 (1973)

$$(4I_3-I_2)/3 = I + 4D(h_3)^4 + 20E(h_3)^6 + \ldots$$

(equation 5)

The process can now be further extended to eliminate the fourth-order error by combining the last two estimates. This process, known as Richardson's extrapolation, can be repeated any number of times until the approximate integral converges to the desired accuracy. In the program, each "inside" integration is done by Romberg quadrature, with the number of integration points for each subinterval being successively doubled up to seven times, or until the difference between two successive estimates of the values of the integration is smaller than the desired relative accuracy of integration.

The computational details of applying Romberg quadrature to a subinterval are relatively straightforward. A vector S is defined (S(1), S(2), S(3), . . . , S(7)). The variables are suitably transformed so that the integral over the subinterval can be re-expressed in the form:

$$I = \int_0^1 f(y)\,dy$$

(equation 6)

S(1) is assigned the value of an initial trapezoidal rule approximation to this integral:

$$S(1) \leftarrow (f(0)+f(1))/2 \simeq I \qquad \text{(equation 7)}$$

We then proceed with the first step of Richardson's extrapolation

$$S(2) \leftarrow S(1) + f(0.5) \simeq 2I \qquad \text{(equation 8)}$$

$$S(1) \leftarrow (2S(2) - S(1))/3 \simeq I \qquad \text{(equation 9)}$$

This new approximation is compared with the previous value of S(1) If convergence has not been achieved, another step of Richardson's extrapolation is performed, with double the number of function evaluations:

$$S(3) \leftarrow S(2) + f(0.25) + f(0.75) \simeq 4I \qquad \text{(equation 10)}$$

$$S(2) \leftarrow (2S(3) - S(2))/3 \simeq 2I \qquad \text{(equation 11)}$$

$$S(1) \leftarrow (8S(2) - S(1))/15 \simeq I \qquad \text{(equation 12)}$$

This process is continued until convergence to the desired accuracy.

In the case of the "outside" integrals, those with limits 1 and ∞, it was found that no appreciable improvement to the accuracy could be achieved by applying Richardson's extrapolation. This is because, as the article by Handy and Boys[108] explains, the values of the first few derivatives of the function at the end points are zero or very small. In terms of our previous notation, the values of C and D are very small, and eliminating them by Richardson's extrapolation does not have a significant effect on the accuracy of the integral. On the other hand, these kinds of integrals are now very sensitive to a reduction of the mesh size h_1. The number of function evaluations can be set to the smallest value that achieves the desired accuracy. Since Romberg quadrature is not being applied, the number of function evaluations need not be a power of 2.

These "outside" integrals are of the form:

$$I = \int_1^\infty g(x)\,dx \qquad \text{(equation 13)}$$

and are transformed, using

$$x = (5/p)(1-p)^4 + 1 \qquad \text{(equation 14)}$$

$$dx = (1-x)(3p+1)/(p-p^2)\ dp$$

(equation 15)

to

$$I = -\int_0^1 g(x(p))\ (dx(p)/dp)\ dp$$

(equation 16)

This transformation of coordinates tends to "flatten" the integrand by reducing the values of the first few derivatives near the end points, while at the same time resulting in suitable subintervals, allowing for rapid convergence of the "inside" integrations. Re-expressing the above integral as:

$$I = \int_0^1 h(p)\ dp$$

(equation 17)

and keeping in mind the fact that the value of the function h(p) is zero at p=1 and p=0, the trapezoidal rule quadrature for this integral is simply:

$$I \approx 1/k \sum_{i=1}^{k-1} h(i/k)$$

(equation 18)

Approximately 50 points are necessary for the evaluation of the "outside" integrals to an accuracy of 8 figures. The values of several of the integrands are negligible relative to the definite integral near the end points, and are not evaluated. Some of the segments of the integrals can be more easily evaluated by an approximate method, as will be discussed later.

The integrand g(x) described above can contain one or more of the three following "inside" numerical integrations:

$$\int_x^\infty G_{ab}(y)\ K_{ab}(y)\ dy$$

(equation 19)

$$\int_x^\infty Q_{bc}(y)\ W_{cd}(y) \cdot h_c(y)\ dy$$

(equation 20)

$$\int_x^\infty Q_{ab}(y)\ Q_{bc}(y)\ h_b(y)\ dy$$

(equation 21)

The values of the integrand of the "outside" integral are evaluated in order of decreasing value of the abscissa. It is therefore possible, when a value of the "inside" integral is required over the interval x(i) to ∞, to numerically integrate

between the limits x(i) and x(i-1) (x(i) < x(i-1)), and add this to the previously calculated integral whose lower integration limit was x(i-1). In the program, all of the multielectron integrals in $\mathcal{E}$ are calculated simultaneously, and it is therefore not necessary to store the values of the integrands or any other intermediate values at different mesh points. The value of the integral for the highest finite value of x(i) is approximated as zero in most cases, unless it is easily estimated.

The value of the integral:

$$I(x) = \int_x^\infty G_{ab}(y) K_{ab}(y)\, dy \qquad \text{(equation 22)}$$

can be approximated as

$$-[Q_{l_{ab}}^{|m_{ab}|}(x) / P_{l_{ab}}^{|m_{ab}|}(x)] K_{ab}(x) \qquad \text{(equation 23)}$$

This approximation holds in those cases where

$$K_{ab}(x) \simeq K_{ab}(\infty)$$

(equation 24)

For instance, in those cases where m =0 and l =0, this expression reduces to:

$$\int_x^\infty (1-y^2)^{-1} \int_1^y z^{j_b} e^{-\alpha_b z} \, dz \, dy$$

(equation 25)

or linear combinations of such functions. For large enough x, this integral is accurately approximated by:

$$\int_x^\infty (1-y^2)^{-1} \{\int_1^\infty z^{j_b} e^{-\alpha_b z} \, dz\}$$

(equation 26)

This integral can be evaluated analytically, since

$$\int_x^\infty (1-y^2)^{-1} \, dy = -\left(\frac{1}{x} + \frac{1}{3x^2} + \frac{1}{5x^5} + \ldots \right) = -Q_0(x)$$

(equation 27)

and integral $K_{ab}(x)$

is used extensively in the program. Its method of evaluation, as well as that of the associated Legendre function of the second kind, are in the next section.

In only one case is it necessary to evaluate a triple integral. Integral $\langle r_{ab}^{-1} r_{bc}^{-1} r_{cd}^{-1} \rangle$ in ε has an inside integral which contains a "W" function which is itself evaluated by a numerical integration. An interpolation is used for these values. What is needed is the integration over the limits (c, ∞) of a given function of type $G(x)K(x)$, for values of c between a and b. We have already calculated the integrals of $G(x)K(x)$ over the limits (b, ∞) and (a, b), using as many values of $G(y)K(y)$ $(a<y<b)$ as were necessary to achieve convergence of the Romberg quadrature. The approximation used is essentially a trapezoidal rule quadrature over the limits (y, b), scaled to make the quadrature equal to the value found by Romberg quadrature over the limits (a, b).

The K integrals and associated Legendre functions

The K integrals to be evaluated are of the form

$$K(y) = \int_1^y (x^2-1)^{m/2}\, P_l^m\,(x)\, x^j\, e^{-\alpha x}\, dx \quad ; 1 \leq y < \infty$$

(equation 30)

and can be evaluated analytically at the same time as values of the associated Legendre function of the first kind. Using the expansion for a Legendre function[109] with x real argument x > 1 in terms of a hypergeometric function:

$$P_l^m\,(x) = \frac{(l+m)!}{(l-m)!\,m!}\left(\frac{x-1}{x+1}\right)^{m/2} F(-l,\ l+1;\ m+1,\ \frac{1-x}{2}\ )$$

(equation 31)

where the hypergeometric function F(a, b; c, d) is given by the finite series

$$F(a,b;c,x) = 1 + \frac{a\,b}{c\ 1!}\,x^1 + \frac{a(a+1)\ b\,(b+1)}{c(c+1)\ 2!}\,x^2 + \frac{a(a+1)(a+2)\ b\,(b+1)(b+2)}{c(c+1)(c+2)\ 3!}\,x^3 + \ldots$$

(equation 32)

we see that the integral becomes

$$K(y) = \frac{(l+m)!}{(l-m)!\ m!}\int_1^y x^j e^{-\alpha x}(x-1)^m F(-l, l+1; m+1, (1-x)/2)\ dx$$

(equation 33)

The integrals can therefore be expressed in terms of the simpler integrals:

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[109] T. M. MacRobert, "Spherical Harmonics", 3rd edition, p. 115, Pergamon Press, Oxford, 1967

$$K(y) = \Sigma C_k \int_1^y x^j e^{-\alpha x} (x-1)^k \, dx$$

(equation 34)

where the coefficients C_k come from the expansion of the associated Legendre function as a hypergeometric function. Using the binomial expansion for $(x-1)^k$, the integrals can be further reduced to the form:

$$K(y) = \Sigma C_k I^{\alpha}_{j+1}(y)$$

(equation 35)

where

$$I^{\alpha}_{j}(y) = \int_1^y x^j e^{-\alpha x} \, dx$$

(equation 36)

These integrals are easily evaluated analytically. The expression for them is

$$I^{\alpha}_{j}(y) = j! \sum_{r=0}^{j} \frac{e^{-\alpha} - e^{-\alpha y} y^{j-r}}{(j-r)! \, \alpha^{r+1}}$$

(equation 37)

This may be re-expressed as:

$$I_j(y) = S_j(1) - S_j(y)$$

(equation 38)

where

$$S_j^{\alpha}(y) = \frac{j!}{\alpha^{j+1}} e^{-\alpha y} (\alpha y)^0 + \frac{\alpha y}{1!} + \frac{(\alpha y)^2}{2!} + \dots + \frac{(\alpha y)^j}{j!}]$$

(equation 39)

When j is small, this expression is easily evaluated. When j is large, however (the program uses j = $\alpha y+4$ as the approximate cutoff), it can be quicker to use a different expression obtained thus:

$$e^{\alpha y} = 1 + \frac{\alpha y}{1!} + \frac{(\alpha y)^2}{2!} + \dots$$

(equation 40)

$$S_j^{\alpha}(y) = \frac{j!}{\alpha^{j+1}} e^{-\alpha y} e^{\alpha y} - [\frac{(\alpha y)^{j+1}}{(j+1)!} + \frac{(\alpha y)^{j+2}}{(j+2)!} + \dots]$$

(equation 41)

$$= \frac{j!}{\alpha^{j+1}} - e^{-\alpha y} \frac{(\alpha y)}{(j+1)} + \frac{(\alpha y)}{(j+1)(j+2)} + \dots$$

(equation 42)

For large enough j, this infinite sum converges quickly to the required accuracy.

Looking at the definition of $S_j^{\alpha}(y)$, it is evident that

$$\lim_{y\to\infty} S_j^{\alpha}(y) = 0$$

(equation 43)

This means that

$$\int_y^\infty x^j e^{-\alpha x} dx = S_j^\alpha(y)$$

(equation 44)

and

$$\int_1^\infty x^j e^{-\alpha x} dx = S_j^\alpha(1)$$

(equation 45)

For values of x very close to 1.0, and many such values are required in the calculation, steps must be taken to avoid the reduction in the accuracy of the numerical methods due to catastrophic cancellation. This problem can be especially severe for integrals involving associated Legendre functions having nonzero values of m. In each of the steps necessary to produce "K" integrals out from linear combinations of "I" integrals, and I_j^α (y) integrals from the integrals S_j^α (1) and S_j^α (y), one is subtracting very similar numbers and losing several significant figures at each step. It can be shown that for $x = 1+\delta$, where $\delta \ll 1$, the integral I can be obtained directly as the expansion

$$I_j^\alpha(1+\delta) = e^{-\alpha}[\delta - \frac{\delta^2}{2}(\alpha-j) + \frac{\delta^3}{6}(\alpha^2-2j\alpha+j(j-1)) - \frac{\delta^4}{24}(\alpha^3-3j\alpha^2+3j(j-1)\alpha-j(j-1)(j-2))]$$

(equation 46)

Since all of the K integrals at a given mesh point y are evaluated at the same time, the program proceeds, for each new value of y, by evaluating all the necessary values of $I_j^{*}(y)$, then combines them using a binomial expansion to give all required values of the integral

$$\int_1^y x^j e^{-\alpha x}(x-1)^k dx$$

(equation 47)

These integrals are then combined, using the coefficients from the hypergeometric expansion of the associated Legendre polynomials of the first kind, to give the values of the K integrals at the mesh point y.

Associated Legendre Functions of the Second Kind

Of those methods attempted, the most rapidly convergent expansion for this function over the required range of $(1,\infty)$ has been found to be[110]

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[110] MacRobert P. 295; I.A. Stegun, "Legendre Functions" 8.10.15, in "Handbook of Mathematical Functions" (M. Abramowitz, I.A. Stegun ed.) Dover, New York, 1965

$$Q_l^m(x) = \frac{(l+m)!}{\Gamma(l)}\left[\frac{\pi}{2(x^2-1)^{1/2}}\right]^{1/2}\left[x-(x^2-1)^{1/2}\right]^{l+1/2}$$

$$F\left(m+\frac{1}{2}, \frac{1}{2}-m; l+\frac{3}{2}, \frac{(x^2-1)^{1/2}-x}{2(x^2-1)^{1/2}}\right)$$

(equation 48)

Using the relation

$$\Gamma(l) = (l+\frac{3}{2}) = \frac{(2l+1)!!}{2^{l+1}}(\pi)^{1/2}$$

(equation 49)

and the new variables

$$y = (x^2-1)^{1/2}$$

(equation 50)

$$z = (x/y - 1)$$

(equation 51)

the expansion reduces to

$$Q_l^m(x) = \frac{(l+m)!}{(2l+1)!!}[2z]^{1/2}[2yz]^{l}F\left(m+\frac{1}{2}, \frac{1}{2}-m; l+\frac{3}{2}, -z/2\right)$$

(equation 52)

This hypergeometric series is an infinite series, but a rapidly convergent one for values of x that are not very close to 1. A more general procedure, and one which is quicker for small values of x, is recursion from the initial value:

$$Q_0^0(x) = \frac{1}{2} \ln\left(\frac{x+1}{x-1}\right) = 1/x + 1/3x^3 + 1/5x^5 + \ldots$$

(equation 53)

The recursion for higher values of m is based on the recurrence relation:

$$(2l+1)(x^2-1)^{1/2} Q_l^{m+1}(x) = (l+m)(l+m+1)Q^m_{l-1}(x) - (l-m)(l-m+1)Q^m_{l+1}(x)$$

(equation 54)

while recursion for higher l is based on the relation:

$$(2l+1)xQ_l^m(x) = (l+m)Q^m_{l-1}(x) + (l-m+1)Q^m_{l+1}(x)$$

(equation 55)

It should be noted that upward recursion may be unstable in this case, but with sufficiently accurate initial values and few enough steps in the recursion, this does not present a problem.

Clebsch-Gordan Coefficients

There exist many different definitions for the Clebsch-Gordan coefficients, depending on whether they refer to spherical harmonics, normalized, or unnormalized Associated Legendre polynomials. The method used will be based on that of Harris and Michels[111], and their definition will therefore be used:

$$P_j^\sigma(x)\,P_k^\tau(x) = \sum_\mu C_{\mu,j,k}^{\sigma,\tau}\, P_\mu^{\sigma+\tau}(x)$$

(equation 56)

The only values required are

$$C_{\mu,j,k}^{\sigma,\tau} = C_{\mu,k,j}^{\tau,\sigma}\,; \quad \tau \geq \sigma \geq 0$$

(equation 57)

Recursion relations between the coefficients can be found using the relation

$$(2l+1)\,xP_l^m(x) = (l+m)\,P_{l-1}^m(x) + (l-m+1)\,P_{l+1}^m(x)$$

(equation 58)

Placing this into the equation:

$$(xP_k^\tau(x))\; P_{j-1}^\sigma(x) = P_k^\tau(x)\;(xP_{j-1}^\sigma(x))$$

(equation 59)

we obtain the relation:

$$P_{j-1}^\sigma(x)\left[\frac{k-\tau+1}{2k+1}P_{k+1}^\tau(x) + \frac{k+\tau}{2k+1}P_{k-1}^\tau(x)\right] = P_k^\tau(x)\left[\frac{j-\sigma}{2j-1}P_j^\sigma(x) + \frac{j+\sigma-1}{2j-1}P_{j-2}^\sigma(x)\right]$$

(equation 60)

Expressing the products of Legendre polynomials in terms

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[111] F. E. Harris and H. H. Michels, Adv. Chem. Phys. vol. 13, p. 205 (I. Prigogine ed.) Interscience, New York (1967)

of Clebsch-Gordan coefficients gives the relation

$$\frac{k-\tau+1}{2k+1}\sum_{\mu} C^{\sigma,\tau}_{\mu,j-1,k+1} P^{\pi}_{\mu}(x) + \frac{k+\tau}{2k+1}\sum C^{\sigma,\tau}_{\mu,j-1,k-1} P^{\pi}_{\mu}(x) =$$

$$\frac{j-\sigma}{2j-1}\sum_{\mu} C^{\sigma,\tau}_{\mu,j,k} P^{\pi}_{\mu}(x) + \frac{j+\sigma-1}{2j-1}\sum C^{\sigma,\tau}_{\mu,j-2,k} P^{\pi}_{\mu}(x)$$

(equation 61)

where $\pi = \sigma+\tau$. Since the Legendre functions are linearly independent, we conclude that

$$\frac{k-\tau+1}{2k+1} C^{\sigma,\tau}_{\mu,j-1,k+1} + \frac{k+\tau}{2k+1} C^{\sigma,\tau}_{\mu,j-1,k-1} =$$

$$\frac{j-\sigma}{2j-1} C^{\sigma,\tau}_{\mu,j,k} + \frac{j+\sigma-1}{2j-1} C^{\sigma,\tau}_{\mu,j-2,k}$$

(equation 62)

If, instead of expanding the right hand side of the original equation, we were to expand the product of Legendre polynomials in terms of Clebsch-Gordan coefficients, we would obtain the relation

$$xP^{\tau}_{k}(x)\ P^{\sigma}_{j-1}(x) = x\sum_{\nu} C^{\sigma,\tau}_{\nu,j-i,k} P^{\pi}_{\nu}(x)$$

$$= \sum_{\nu} C^{\sigma,\tau}_{\nu,j-1,k} \frac{\nu+\pi}{2\nu+1} P^{\pi}_{\nu-1}(x) + \sum_{\nu} C^{\sigma,\tau}_{\nu,j-1,k} \frac{\nu-\pi+1}{2\nu+1} P^{\pi}_{\nu+1}(x)$$

(equation 63)

Combining this with the expanded left hand side of the original equation, and adjusting the summations, we obtain:

$$\frac{k-\tau+1}{2k+1}\sum_{\mu}C^{\sigma,\tau}_{\mu-1,j-1,k+1}P^{\pi}_{\mu-1}(x) + \frac{k+\tau}{2k+1}\sum_{\mu}C^{\sigma,\tau}_{\mu-1,j-1,k-1}P^{\pi}_{\mu-1}(x) =$$

$$\sum_{\mu}\frac{\mu+\pi}{2\mu+1}C^{\sigma,\tau}_{\mu,j-1,k}P^{\pi}_{\mu-1}(x) + \sum_{\mu}\frac{\mu-\pi-1}{2\mu-3}C^{\sigma,\tau}_{\mu-2,j-1,k}P^{\pi}_{\mu-1}(x)$$

(equation 64)

Since the Legendre polynomials are linearly independent, this relation reduces to:

$$\frac{\mu+\pi}{2\mu+1}C^{\sigma,\tau}_{\mu,j,k} + \frac{\mu-\pi-1}{2\mu-3}C^{\sigma,\tau}_{\mu-2,j,k} = \frac{k+\tau+1}{2k+1}C^{\sigma,\tau}_{\mu-1,j,k+1} + \frac{k+\tau}{2k+1}C^{\sigma,\tau}_{\mu-1,j,k-1}$$

(equation 65)

It should be noted that the Harris and Michels version of this relation (equation 152) is in error.

In order to use this recursion scheme, we need the initial values of

$$C^{\sigma,\tau}_{\pi,\sigma,\tau} \; ; \; C^{\sigma,\tau}_{\pi,\sigma,\tau+2} \; ; \; C^{\sigma,\tau}_{\pi,\sigma,\tau+4} \; ; \; \ldots \; ; \; C^{\sigma,\tau}_{\pi,\sigma,\tau+2\sigma}$$

(equation 66)

This can be done by using the integral[112]

$$\int_{-1}^{1}P^{u}_{l}(x)\,P^{v}_{m}(x)\,P^{n}_{n}(x)\,dx = (-1)^{s-1}\,2\,\frac{(l+u)!\,(m-v)!\,(2n)!\,(2s-2n)!\,s!}{(s-1)!\,(s-m)!\,(s-n)!\,(2s+1)!}$$

$$u = v+n \; ; \; l+m+n = 2s \; ; \; m+n \geq l \geq m-n \; ; \; l \geq u \; ; \; l \geq n-m$$

(equation 67)

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[112] J. A. Gaunt, Phil. Trans. Roy. Soc. Lon. (A) <u>228</u>, 151 (1929)

The following integral can be expressed in two ways

$$\int_{-1}^{1} P_{\sigma+\tau}^{\sigma+\tau}(x)\, P_{\tau+2\sigma-2k}^{\tau}(x)\, P_{\sigma}^{\sigma}(x)\, dx =$$

$$(-1)^{\tau+k+1} 2 \frac{(2\sigma-2k)!\,(2\sigma)!\,(2\sigma+2\tau-2k)!\,(2\sigma+\tau-k)!}{(\sigma+\tau-k)!\,(\sigma-k)!\,k!\,(4\sigma+2\tau-2k+1)!}$$

$$= \frac{2}{2(\sigma+\tau)+1}\,(2\sigma+2\tau)!\; C_{\sigma+\tau,\,\sigma,\,\tau+2\sigma-2k}^{\sigma,\,\tau}$$

$$;\quad 0 \le k \le \sigma \quad .$$

(equation 68)

where k is in the range $(0, \sigma)$. We now have an explicit expression for the initial values that we were looking for, namely:

$$C_{\sigma+\tau,\,\sigma,\,\tau+2\sigma-2k}^{\sigma,\,\tau} = (-1)^{\tau+k+1} \frac{(2\sigma+2\tau+1)(2\sigma-2k)!\,(2\sigma)!\,(2\sigma+2\tau-2k)!\,(2\sigma+\tau-k)!}{(\sigma+\tau-k)!\,(\sigma-k)!\,k!\,(4\sigma+2\tau-2k+1)!}$$

(equation 69)

The procedure for evaluating the Clebsch-Gordan coefficients is simple. For given values of σ and τ , we start with the initial values described above, and raise the values of μ and k, keeping $j = \sigma$, then raise the values of j. It must be kept in mind that the Clebsch-Gordan coefficient

$$C_{\mu,\,j,\,k}^{\sigma,\,\tau}$$

(equation 70)

will be zero if $j = |\sigma| - 1$, or $k = |\tau| - 1$, or if $\mu+j+k$ is not even, or $\mu < |j-k|$, or $\mu > j+k$. Note also that coefficients are required only for positive values of σ and τ

Integral storage

The only integrals that were stored were the integrals of type II and those of type IV. The others were computed as needed and not stored, because of the number and variety of such integrals.

Integrals of type II,

$$\int_1^\infty h_a(x)\,W_{ab}(x)\,dx \qquad \text{(equation 71)}$$

can be stored using two indices, one representing one of the 120 possible types of h_a and the other standing for one of the 10200 allowed forms of W_{ab}.

Integrals of type IV,

$$\int_1^\infty h_a(x)\,W_{ab}(x)\,W_{ac}(x)\,dx \qquad \text{(equation 72)}$$

can be stored using three indices, one representing one of the 120 possible types of h_a as before, and the other two interchangeable indices each standing for one of the 10200 allowed forms of W_{ab} and W_{ac}.

In both these cases, the indices used to identify the integrals that need to be calculated are the same as those used to identify the stored integrals. The stored integrals are sorted into lexicographic order according to these indices, and are retrieved from the list using a search order found by bisection or linear interpolation of the indices. By whatever method, the search for these stored integrals is one of the more time-consuming parts of the program.

Integrals of type V are similarly identified using one index for h, and three indices for W_{ab}, W_{ac}, and W_{ad}. Integrals of type VI use two indices for h, two indices for W, and another index to identify the Associated Legendre Functions, of which there are 85 allowed forms. The two pairs of h and W are interchangeable. Integrals of type VII are identified by three interchangeable indices, each representing the combination of a P and an h index.

All integral "requests", requests being sets of indices that tell the integration program which integrals need to be evaluated, also consist of another integer index indentifying the matrix element from which the request originates, and a real number by which the integral is to be multiplied before being added to the matrix element in question.

In the main program, the integral requests are stored and the real factor updated using combined chained list hashing[113] to determine the addresses at which the requests are stored and the search order by which they are retrieved. Briefly, this method is used to calculate a pseudo-random but reproducible address for each integral request, from its indices. These calculated addresses are known as hash codes, and the function that generates them usually involves a modulus. If it finds the address already occupied by a request, it checks whether it corresponds to the same integral, in which case it simply adjusts the factor by which this integral is to be multiplied. If the request is for a different integral, it checks the value of a pointer which will direct it to the next possible address in the chain, until a previous request for the same integral is located, or until the end of the chain is reached and the pointer has no value. If it is the case, it sets this last pointer to the lowest unoccupied address, and there writes the request. Alternatively, if somewhere along the chain an integral request has been encountered with a zero (or very small) factor, this new request can take its place in the middle of the chain rather than at the end. Since there is only one set of pointers, all the addresses in a given chain will not

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[113] C.C. Gotlieb, L.R. Gotlieb, "Data Types and Structures", Prentice-Hall, New York, 1982, Ch. 4

necessarily have had the same hash code (calculated pseudorandom address), but could also have one that corresponds to other addresses later in the chain. The chains for each of the calculated addresses are thus said to be combined. This makes the length of the search a little longer, but saves a great deal of space.

Whenever a list of such requests seems to be full, or when no more integrals are needed in a given matrix element, the program "condenses" the list. All the empty addresses as well as those with a zero (or very small) factor are deleted from the list, and the others are moved to the beginning of the list. The pointers are all set to zero, and the empty part of the list is now treated as though it were a new, shorter list. We call this process "masking" of the integral requests. The speed of combined chained list hashing depends very much on the ratio of empty to occupied addresses in the list.

Second spin function

The second spin function was automatically calculated wherever it had a nonzero value, leaving the matrix diagonalisation program the option of using it or not. The only exception was for basis functions that included an odd power of one of the interelectronic distances.

Since the second spin function only gives non-zero matrix elements when the number of distinct permutations of the configuration is high, the number of distinct integrals required to calculate these matrix elements is also high. In this case, the amount of extra space required to deal with the integrals required for the second spin function was thought not to be justified by the small energy contribution expected from these extra configurations. They were therefore not calculated.

CHAPTER 6

PROPERTIES TO BE CALCULATED

The program has been designed so that many expectation values and properties could be derived from the wavefunction. As was mentioned in an chapter 4, the matrix representation in the chosen basis, of five different even operators and two odd operators is calculated. These operators, defined earlier, are S(g), V(g), T(g), Q(g), R(g), V(u), and D(u). These operators are calculated for one given internuclear distance (generally 2.0 bohr), but can be scaled to any given distance by the use of the appropiate scaling factor.[114] If the matrix elements have been calculated for an internuclear separation of 2.0 bohr, then in order to obtain the correct matrix at an internuclear separation of R, the T(g) matrix will have to be multiplied by $(2.0/R)^2$, the V(g) and V(u) matrices by (2.0/R), the D(u) matrix by (R/2.0), and the R(g) and Q(g) matrices by $(R/2.0)^2$.

For a given set of configurations, there exists a scaling

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[114] A.D. McLean, J. Chem. Phys. 40, 2774 (1964)

factor and therefore an internuclear distance for which the eigenvalue of the Hamiltonian is minimized. At this distance, the wavefunction will obey the virial theorem[115], which states that

$$-\langle V\rangle / (2\langle T\rangle) = 1 \qquad \text{(equation 1)}$$

where $\langle V\rangle$ is the expectation value of the potential energy operator and $\langle T\rangle$ that of the kinetic energy operator for the given eigenfunction of the Hamiltonian operator. It must be noted that it is not sufficient to multiply the interelectronic distance by the calculated virial coefficient, since the variationally determined energy may very well be lower when the linear variational parameters are re-optimized after having optimized the distance. The linear parameters and scale factor can thus be optimized in turn until the virial coefficient is equal to one, or alternatively the scale factor can be linearly extrapolated to a value which makes the virial coefficient of the variationally optimized eigenfunction equal to one.

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[115] P. Phillipson, J. Chem. Phys. 39, 3010 (1963); C.A. Coulson and A.C. Hurley, J. Chem. Phys. 37, 449 (1962) and 37, 488 (1962); G.C. Hall, Phil. Mag. 6, 249 (1961); Cottrell and Patterson, Trans. Far. Soc. 47, 233 (1951); Coulson and Bell, Trans. Far. Soc. 41, 141 (1945); W.L. Clinton, J. Chem. Phys. 33, 1603 (1933); see also J. Goodisman, "Diatomic Interaction Potential Theory", pp. 195-241, Academic Press, New York, 1973

By combining available matrices, one can obtain useful eigenfunctions and expectation values. By adding together the matrices V(g)+V(u)+T(g) and using the overlap matrix S(g), one can obtain eigenvectors and eigenvalues of the matrix representation of the Hamiltonian operator, using standard programs such as CEIG[116] and GIVENS[117] or EISGIV.[118] A field-perturbed Hamiltonian can be created by adding to the Hamiltonian matrix a constant (equal to the field in atomic units) times the D(u) matrix. A field gradient can be added by adding to the Hamiltonian a constant times the quadrupole moment operator matrix(discussed below). These perturbed eigenfunctions can be used to derive the axial part of the polarizability tensor.

Many properties can be derived from the expectation values values of the available matrices. The following formulae will apply specifically to four-electron diatomic molecules, although some are more general.

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[116] Quantum Chemistry Program Exchange, program 97, Department of Chemistry, Indiana University, Bloomington

[117] Quantum Chemistry Program Exchange, program 62, Department of Chemistry, Indiana University, Bloomington

[118] Part of the package EIGLIB

The dipole moment can be derived by subtracting the expectation value of the operator represented by matrix D(u) from the dipole moment caused by the point charges of the nuclei. When the molecule is uncharged, the dipole moment does not depend on the origin chosen, although the electronic and nuclear contributions to it alone are not gauge independent. The expectation value $\langle z \rangle$, measured from the center of mass of the nuclei, is found by subtracting from the expectation value of D(u) the distance δ from the coordinate origin (the midpoint between the nuclei) to the center of mass. The center of mass is calculated by using the masses of the most abundant isotopes of the nuclei. In the case of Li and H, these are 7.016 and 1.007825 a.m.u.

The expectation value $\langle z^2 \rangle$, measured from the coordinate origin, is simply the expectation value of the matrix Q(g). To shift this to the center of mass, one must use the transformation:

$$\langle z^2 \rangle_{cm} = \langle z^2 \rangle + 2\delta \langle z \rangle + 4\delta^2$$

(equation 2)

The expectation value of the matrix R(g) gives the value of:

$$\langle r_A^2+r_B^2\rangle/2$$

(equation 3)

which is the expectation value of the average of the square of the distance from nucleus "A" to the electron and of the square of the distance from nucleus "B" to the electron. The expectation values of the square of the distances from nucleus "A", from nucleus "B", and from the coordinate origin are therefore

$$\langle r_A^2\rangle = \langle r_A^2+r_B^2\rangle/2 + 2\langle z\rangle$$
$$\langle r_B^2\rangle = \langle r_A^2+r_B^2\rangle/2 - 2\langle z\rangle$$
$$\langle r^2\rangle = \langle r_A^2+r_B^2\rangle/2 - R^2 = \langle x^2+y^2+z^2\rangle$$

(equation 4)

These expectation values, like most others, are summed over all electrons.

One also gets the obvious result that

$$\langle x^2+y^2\rangle = \langle x^2+y^2+z^2\rangle - \langle z^2\rangle$$

(equation 5)

One can also simply derive the value of the Larmor term of the diamagnetic susceptibility[119] by using the approximate relation:

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[119] A. D. McLean and M. Yoshimine, J. Chem. Phys. 45, 3676 (1966), and 47, 3256 (1967)

$\zeta = (-e^2/6mc^2)\langle r^2\rangle$

where the first value in brackets is a conversion factor for atomic units, equal to 7.91984×10^{-7} erg G^{-2} $mole^{-1}$. It must be noted that the expectation value $\langle r^2\rangle$ should be measured from the electronic centroid (the origin which minimizes its value, coincident in this case with one at which $\langle z\rangle$ is zero), rather than from the center of mass.

One also wishes to calculate the quadrupole moment of the molecule. The quadrupole moment can be calculated by

$$\theta = Z_A d_A^2 + Z_B d_B^2 - \langle z^2 - (x^2 + y^2)/2\rangle$$

(equation 6)

where the first two terms refer to the charges on the nuclei and their distance from the nuclear center of mass. The electronic observables also refer to the nuclear center of mass. This origin is the one from which quadrupole moments are measured experimentally using the diamagnetic anisotropy and rotational g factor[120], but not if they are determined directly from electric field gradient induced birefringence.

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[120] C. J. F. Bottcher and P. Bordewijk, "Theory of Electric Polarization", 2nd ed., vol. II, Elsevier, Amsterdam (1978); A. D. McLean and M. Yoshimine, J. Chem. Phys. 45, 3676 (1966)

It is possible to estimate non-rigorous upper bounds to the dipole polarizabilities[121] by using a method due to Lewis and Dalgarno[122]. According to their reasoning, one can estimate that

$$\alpha_{zz} \leq 2\langle z^2\rangle/(E_A-E_X)$$

$$\alpha_{xx} \leq 2\langle x^2\rangle/(E_B-E_X)$$

(equation 7)

The $\langle z^2\rangle$ is measured form the electronic centroid. The energies of the molecule in the ground (subscript X) state and in the lowest Σ (subscript A) and Π (subscript B) states must be known. In the case of LiH, we have constructed approximate potential curves taken from the data of Bishop and Cheung[87] and that of Partridge and Langhoff.[123]

Approximate energy differences were derived using the relations

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[121] H.E. Montgomery Jr. Chem. Phys. Lett. 56, 307 (1978)

[122] A. Dalgarno and J.T. Lewis, Proc. Roy. Soc. A240, 284 (1957)

[123] H. Partridge and S.R. Langhoff, J. Chem. Phys. 74, 2361 (1981)

$$E_A - E_X = 0.13880 + 0.0269(3-R)$$
$$E_B - E_X = 0.17171 + 0.0251(3-R)$$

(equation 8)

There is no need for greater accuracy. It should be mentioned that the approximation to the upper bound of the polarizabilites depends on the assumption that

$$\langle z_i z_j \rangle \leq 0 \quad , \; i=j$$

(equation 9)

This is intuitively easy to accept, since $\langle z \rangle$ is zero at the electronic centroid and "left-right" correlation would tend to keep pairs of electrons on opposite sides of this point.

Another important property which is estimated is the approximate energy contribution of each of the configurations. It is of course relatively simple to solve the secular equation after having deleted the row and column corresponding to each configuration in turn, but this would be a long and wasteful process. Instead, an approximate upper bound to the energy contribution of each configuration can be calculated[86] using an expression due to Brown. The energy lost by deleting row and column 1 is estimated by:

$$\delta = \frac{|c_1|^2 [H(1,1) - ES(1,1)]}{1 - 2c_1 \Sigma_1 c_1 S(1,1) + c_1^2 S(1,1)}$$

(equation 10)

where c_j is the jth element of the eigenvector, and E is the eigenvalue of the corresponding state. This allows

those configurations which seem to have little effect on the total energy to be deleted.
The estimated energy difference is most reliable for those configurations where this difference is small.

Solving the secular equation for field-perturbed Hamiltonian operators will allow us to calculate the polarizability tensor elements. The polarizabilities other than those along the internuclear axis would require configurations other than those of zero total angular momentum such as are required for the unperturbed Hamiltonian. The solutions of the Hamiltonian perturbed by a field along the internuclear (z) axis span the same Hilbert space as those of the unperturbed Hamiltonian (presuming, of course, that the part of the operator due to the field perturbation be bounded by projection on to the basis of configurations). The field-dependent electronic energy of the system perturbed by a constant field in the z direction and no field gradients can be expanded as:

$$E(F_z) = E(0) - \mu_z F_z - (1/2!)\alpha_{zz} F_z^2 - (1/3!)\beta_{zzz} F_z^3 - (1/4!)\gamma_{zzzz} F_z^4 - \ldots$$

(equation 11)

If the wavefunction obeys the Hellmann-Feynman theorem with respect to distances in the direction of the field, then the expectation value of the dipole moment operator for the solution of the perturbed Hamiltonian can be given by the same coefficients:

$$\mu_z(F_z) = \mu_z(0) + \alpha_{zz}F_z + (1/2!)\beta_{zzz}F_z^2 + (1/3!)\gamma_{zzzz}F_z^3 + \ldots$$
(equation 12)

By calculating the energies and moments of a wavefunction as a function of the field, one can obtain two sets of coefficients corresponding to the polarizabilities. The expressions for the energy and the dipole moment are power series about zero field. The best way to extrapolate the values of the coefficients back to zero field is by using Richardson's extrapolation. This method will eliminate in turn all of the terms in the power series other than the one being calculated. For instance, one can find the first dipole polarizability from the dipole moments by first calculating the two estimates:

$$\alpha_1 = [\mu_z(F_z)-\mu_z(-F_z)]/(2F_z) = \alpha_{zz}+(1/6)\gamma_{zzzz}F_z^2+(1/5!)\varepsilon_{zzzzzz}F_z^4+\ldots$$
$$\alpha_2 = [\mu_z(2F_z)-\mu_z(-2F_z)]/(4F_z) = \alpha_{zz}+(4/6)\gamma_{zzzz}F_z^2+(16/5!)\varepsilon_{zzzzzz}F_z^4+\ldots$$
(equation 13)

These two estimates can be combined to eliminate the second-order error in the polarizability, giving the new estimate:

$$(4\alpha_1-\alpha_2)/3 = \alpha_{zz}-(4/5!)\varepsilon_{zzzzzz}F_z^4 + \ldots.$$
(equation 14)

One can use the difference between the two original estimates of α to estimate the second hyperpolarizability:

$$(\alpha_1-\alpha_2)(2/F_z^2) = \gamma_{zzzz}+(1/4)\varepsilon_{zzzzzz}F_z^2 + \ldots.$$
(equation 15)

The term in ε can be eliminated from two successive second order estimates of the polarizabilities, requiring a total of six fields, and the process can be repeated until satisfactory convergence has been achieved. The process for calculating the odd polarizabilities is analogous. The first dipole polarizability can be estimated in the first order by

$$\beta_1 = (\mu_z(F_z)+\mu_z(-F_z)+2\mu_z(0))/(F_z) =$$
$$= \beta_{zzz}+(2/4!)\delta_{zzzzz}F_z^2+(2/6!)\zeta_{zzzzzzz}F_z^2+\ldots.$$
(equation 16)

Other first order estimates are calculated as before by doubling the field strength, and these are combined to give second order approximations to the polarizabilities:

$$(4\beta_1-\beta_2)/3 = \beta_{zzz}-(1/45)\zeta_{zzzzzzz}F_z^4 + \ldots$$

$$(\beta_1-\beta_2)(4/F_z^2) = \delta_{zzzzz}+(1/6)\zeta_{zzzzzzz}F_z^4 + \ldots$$

(equation 17)

The same methods can be used to derive the electronic part of the dipole moment, and the polarizabilities from the variation of the electronic energy with the field. These values should be the same as those obtained from the dipole moments. From the quadrupole moments, one can obtain the field polarizabilities of the quadrupole moment. These should be equal to the the field gradient polarizabilities of the dipole moment.

Behaviour at the interelectronic cusp

The helium atom wavefunction has, as was discussed in chapter 2, an infinite singularity at the interelectronic cusp. If the wavefunction is written as the product of an uncorrelated function and correlation functions,

$$\Psi = \Phi(r_1, r_2)\sum_{i=0}^{\infty}C_i r_{12}^i$$

(equation 18)

then Tatum's γ_{12} coefficient[12] is given by

$$[(1/\psi)(\partial\psi/\partial r_{12})]_{r_{12}=0} = C_1/C_0$$

(equation 19)

If the wavefunction can not be expressed in such a simple form, then this value will vary with the other electronic coordinates. It will therefore have to be calculated at some specific point, or integrated over the entire wavefunction.

In an N-electron problem, there are N(N-1)/2 such infinite singularities. Since the wavefunction is antisymmetric, the correlation can be expressed only between spin-orbitals rather than between electrons[124], so that the interelectronic cusps are not distinct. The partial derivatives of the wavefunction with respect to the interorbital correlations can be calculated in a manner analogous to the helium atom problem.

In those cases where the wavefunction may be written in the form of the product of function of the interelectronic distances with a function of the other coordinates, the value of the interelectronic cusps is constant over all space, as are the intra- and inter-orbital cusps. The electronic cusps are in fact simple averages of the orbital cusps. In the more general case, interelectronic and

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[124] L. Szasz, Phys. Rev. 126, 169 (1962)

orbital cusps depend on the other coordinates and must generally be integrated over all space. Since the orbitals involved are not orthogonal, the partition of the inter-orbital cusps is not rigorous.

While the wavefunction can not in general be expressed as a product of correlation functions and uncorrelated functions, it is possible to constrain the wavefunction to a similar form of the type:

$$\sum_i a_i \Psi_i (b_{i,0} + b_{i,1} r_{12} + b_{i,2} r_{13} + \ldots + b_{i,7} r_{12}^2 + \ldots)$$

(equation 20)

where some of the "b" coefficients are zero simply because those configurations have not been calculated. We set the condition that

$$\begin{array}{ll} b_{i,k} = b_{j,k} & \text{if the configuration has been calculated} \\ b_{i,k} = 0 & \text{otherwise} \end{array}$$

(equation 21)

and optimize the "a" and "b" coefficients variationally. If the choice of the configurations included in the set has been well made, then the excluded configurations would have had little contribution to the energy.

CHAPTER 7

RESULTS OF THE LiH CALCULATION

Choice of Configurations

As explained previously, it is possible to expand a wavefunction of the form

$$\psi = A[e^{-\alpha_1(\xi_1+\xi_2)} e^{\beta_1(\eta_1+\eta_2)} e^{-\alpha_2(\xi_3+\xi_4)} e^{\beta_2(\eta_3+\eta_4)}] \qquad \text{(equation 1)}$$

as a linear combination of terms of the form

$$\Phi = \sum_k \phi_1(1_1^k,0,0,\alpha_1)\,\phi_2(1_2^k,0,0,\alpha_1)\,\phi_3(1_3^k,0,0,\alpha_2)\,\phi_4(1_4^k,0,0,\alpha_2) \qquad \text{(equation 2)}$$

where the orbitals are defined as in chapter 3, page 57.

By allowing the coefficients of such an expansion to vary freely one can see, by truncating the series after different numbers of terms, that this basis set becomes saturated after about 100-120 terms. The wavefunction is picking up some left-right correlation in the process.

A plot of the reciprocal of the square of the number of basis functions in the expansion versus the lowest eigenvalue of the hamiltonian will give a nearly linear relation. Extrapolation of this line to an infinite number of functions will give the basis set limit for this type of functions, which figure 1 shows to be -7.9867 hartree.

The saturation of the basis set with respect to the dipole and quadrupole moments is also demonstrated in the figures 2 and 3.

The next degree of liberty that can be added to the basis set is, by multiplying the leading terms in the previous expansion by ξ_1 ξ_2 ξ_3 or ξ_4. Since Clary[54] found significant lowering of the energy by adding terms where his "ground" configuration was multiplied by $\xi_3\xi_4$ and by $\xi_1^2\xi_2$, some of the leading terms of our initial expansion were also multiplied by these factors and added to the configuration set.

Clary and other authors have found that a split shell, created by introducing a third nonlinear parameter to the "outer shell" basis set, was necessary for the proper convergence of RHF, UHF, and σ-CI calculations. These types of terms were therefore added. Optimization with a small basis set of uncorrelated functions gave a very

ENERGY CONVERGENCE OF σ-CI

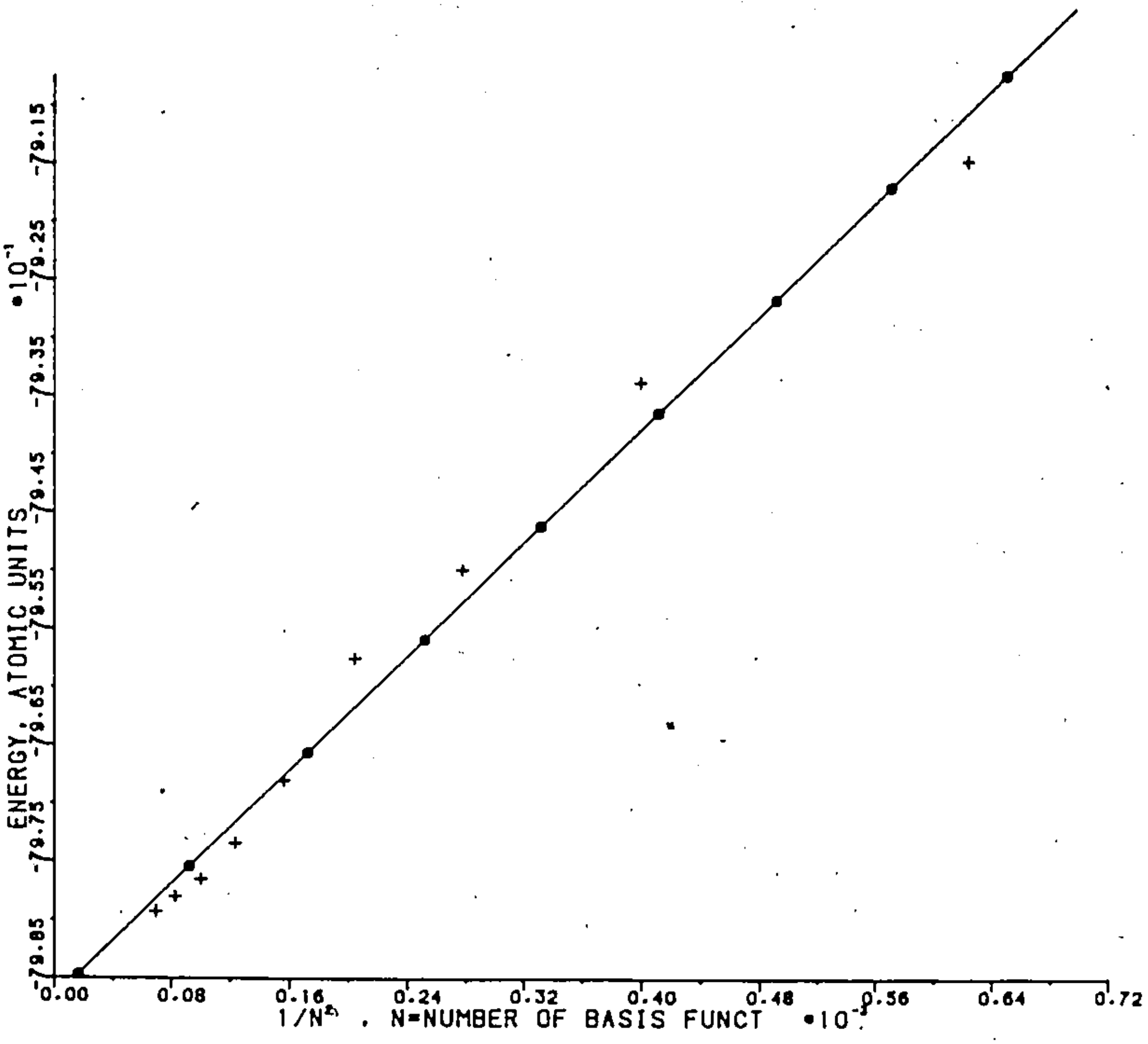

FIGURE 1

DIPOLE MOMENT CONVERGENCE OF σ-CI

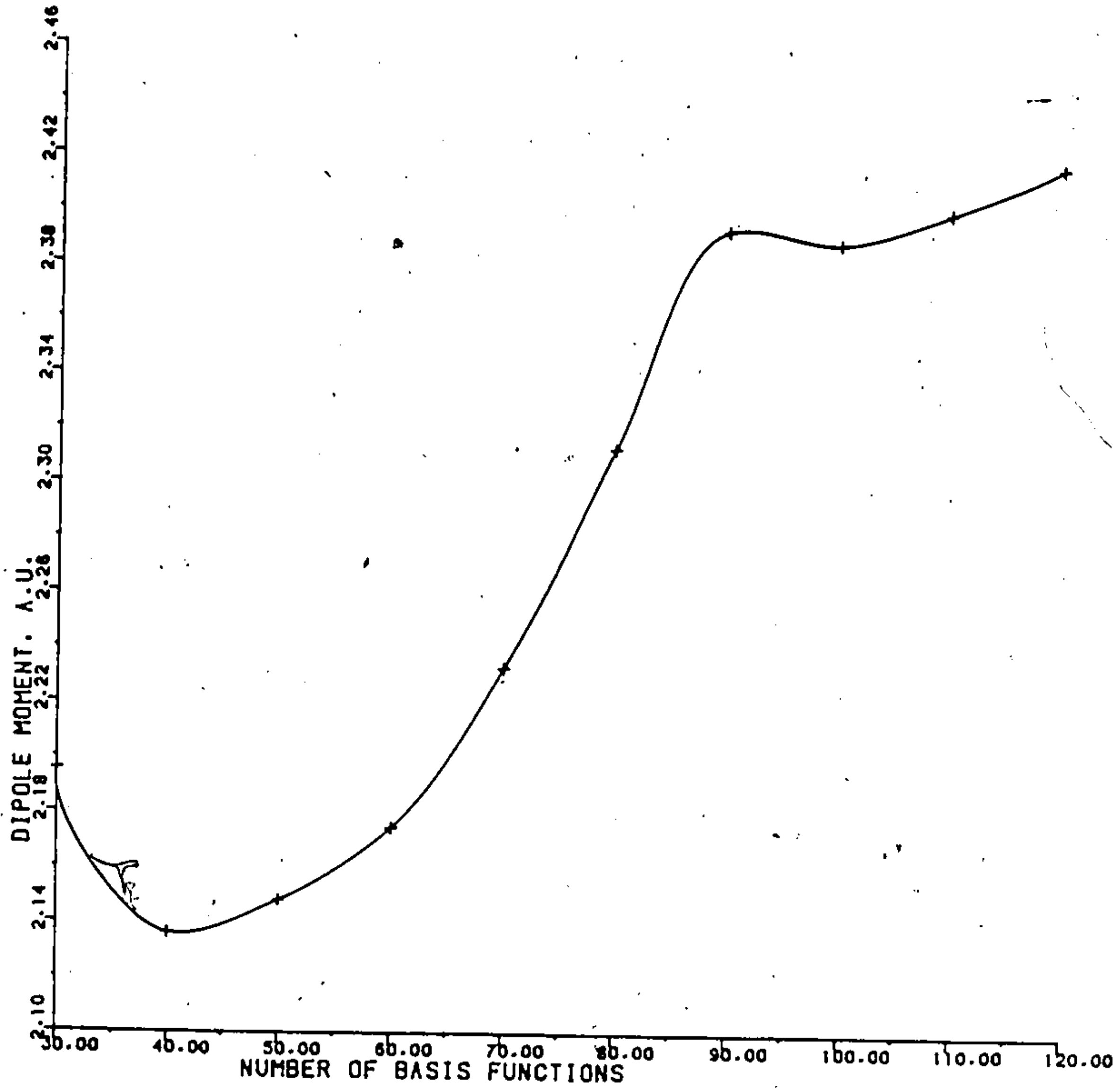

FIGURE 2

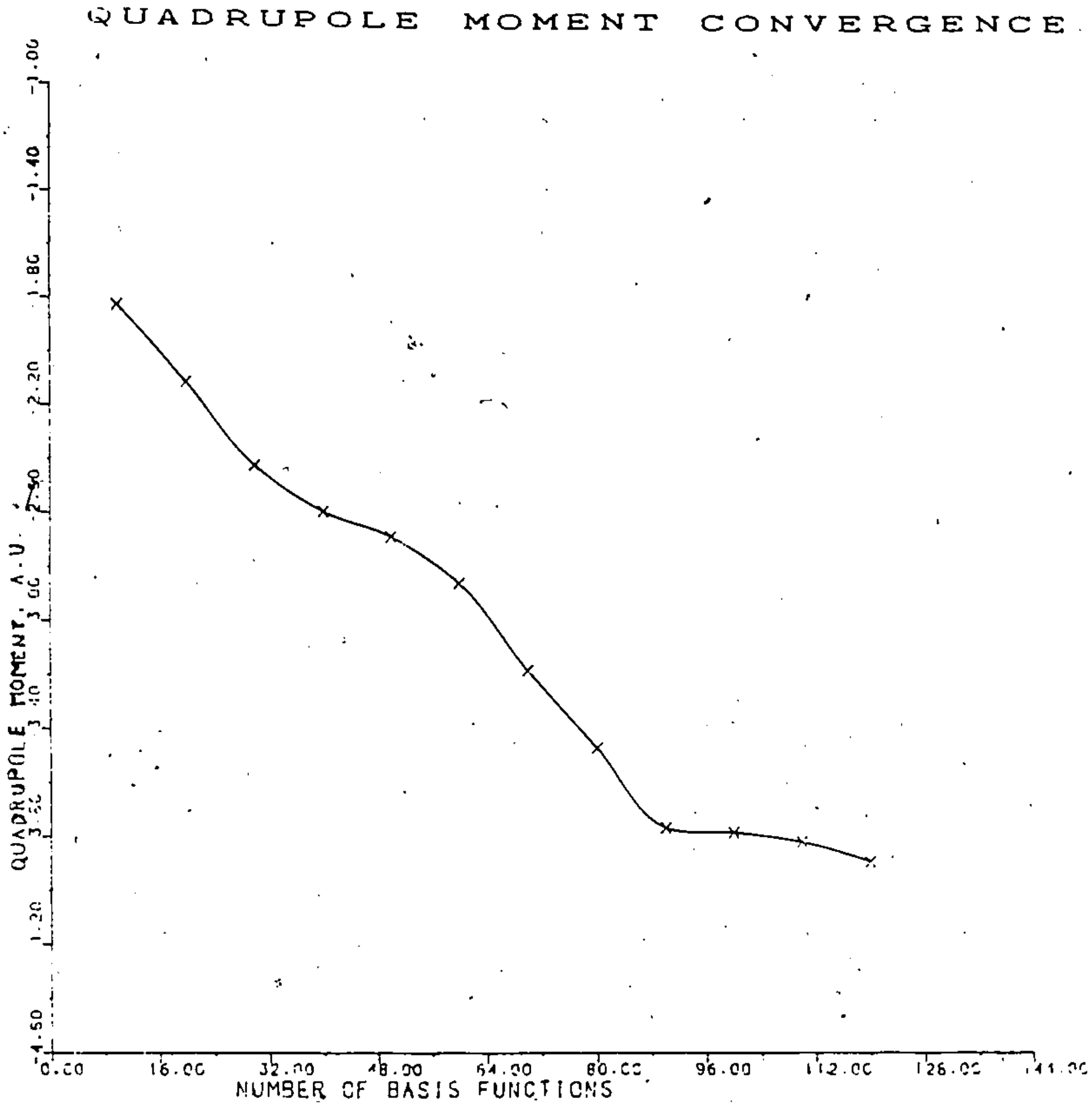
QUADRUPOLE MOMENT CONVERGENCE
QUADRUPOLE MOMENT, A.U.
-1.00
-1.40
-1.80
-2.20
-2.60
-3.00
-3.40
-3.80
-4.20
-4.60
0.00
16.00
32.00
48.00
64.00
80.00
96.00
112.00
128.00
144.00
NUMBER OF BASIS FUNCTIONS

FIGURE 3

shallow minimum near 1.1 . This value was therefore used as our third nonlinear parameter (equations 13 and 19, chapter 3). A wavefunction made up of all the types of configurations discussed so far, none of them explicitly correlated, is called a σ-CI wavefunction.

Since explicitly correlated configurations are expensive to include in the wavefunction, it is useful to be able to predict what the energy lowering will be following their introduction. A few tests seemed to indicate that the energy lowering due to a function of the type:

$$\Phi_a(a)\Phi_b(b)\Phi_c(c)\Phi_d(d)[e^{im(\phi_a-\phi_b)} + e^{im(\phi_b-\phi_a)}]$$

(equation 3)

seems to be a good predictor, and one of the type:

$$\Phi_a(a)\Phi_b(b)\Phi_c(c)\Phi_d(d)r_{ab}^2$$

(equation 4)

an even better predictor of the energy lowering that will result from the addition of a term of the type

$$\Phi_a(a)\Phi_b(b)\Phi_c(c)\Phi_d(d)r_{ab}^1$$

(equation 5)

The configurations with the square of the interelectronic distance were used as predictors, because of the combined effect of the presence of both the first and second powers of the interelectronic distance in the wavefunction, and in

order to more easily calculate the interelectronic cusp. Our final correlated wavefunction is a variational combination of
the configurations in the σ-CI wavefunction and of those configurations involving the first or second power of the interelectronic distances that were found to make a significant contribution to the energy.

The energy of our best σ-CI wavefunction at 3.015 a.u. is -8.0073 hartree, compared with Clary & Handy's value of -8.0316 hartree, or a difference of 0.0243 hartree. The energy of our correlated wavefunction at the same internuclear separation was -8.0395 hartree, compared to the theoretical limit of -8.0705 hartree, or a difference of 0.0310 hartree. One can therefore suppose that most of the missing energy comes not from insufficient correlation but from an insufficient σ-CI wavefunction.

As a rough estimate of the contribution of the explicitly correlated functions to the correlation energy, one can use Clary's assumption that all of the "left-right" and "in-out" correlation has been recovered in a σ-CI calculation, and that the explicitly correlated functions will add the angular correlation. This can be further split into "inner-shell" and "outer-shell" angular correlation and compared to conventional CI estimates of these correlation energies. Since the sum of the individual contributions of the correlation of the two shells does not equal their combined contribution, we chose, for the purpose of comparison, to add inner-shell correlation first, followed by the outer shell.

Table V compares the energy of angular correlation, as defined by the various authors, and is therefore not a direct comparison of well-defined values.

TABLE V
Energy of angular correlation

author	ref.	σ-CI energy	angular correlation	
			inner	outer
Ebbing	80	-8.01554	0.0130	0.0096
Ebbing(estimated)		-8.040	0.0175	0.0106
Bender & Davidson	88	-8.032	0.0170	0.0143
Clary & Handy	83	-8.0316	0.0183	0.0131
this work		-8.0073	0.0220	0.0102

Equilibrium Internuclear Distance

By making use of the virial theorem, one can define the equilibrium internuclear distance of a Born-Oppenheimer wavefunction as that for which the virial ratio $-\langle V\rangle/(2\langle T\rangle)$ is 1.0 . As has been discussed in chapter 3, the nature of the basis set makes it likely that the wavefunction is more accurate for small than for large internuclear distances. If that is the case, then the minimum on the potential curve, which is the equilibrium internuclear distance of the wavefunction, will likely be too low. The equilibrium internuclear distance was found to be 2.8543 for the σ-CI calculation and 2.9039 for the explicitly correlated function. The experimental value of this distance is 3.015 bohr.

Whether the calculated equilibrium distance increases or decreases with the addition of explicitly correlated functions depends on whether the improvement to the wavefunction is greater at longer or shorter distances. The theoretical improvement to the energy possible from the addition of correlated terms may be increased or decreased with internuclear distance, although in the case of LiH, the Hartree-Fock equilibrium internuclear distance is very close to the experimental one[99] , implying that the correlation improvement does not vary much with internuclear distance. How much of that possible energy lowering is retrieved by the limited number of correlated functions probably depends on the basis set's ability to accurately describe the neighbourhood of the interelectronic cusps.

Energy Curves

Even though it is possible, by scaling the kinetic and potential energy operator matrices, to calculate an upper bound to the energy at any internuclear distance, the present calculations make use of the non-linear parameters 4.024 and 1.318, which are probably near-optimal for the equilibrium internuclear distance. The difficulty involved in calculating correlated matrix elements ruled out reoptimizing or rescaling nonlinear parameters at each internuclear distance. The wavefunction can therefore be expected to be best near this equilibrium internuclear distance and to deteriorate away from this point. Comparison of our σ-CI and correlated wavefunction energy curves with the very accurate energy curve of Bishop and Cheung[87] in figure 4 makes this easy to see.

Unfortunately, the nature of the potential curve away from the minimum makes it impossible to report any calculated spectroscopic constants. In the range which we

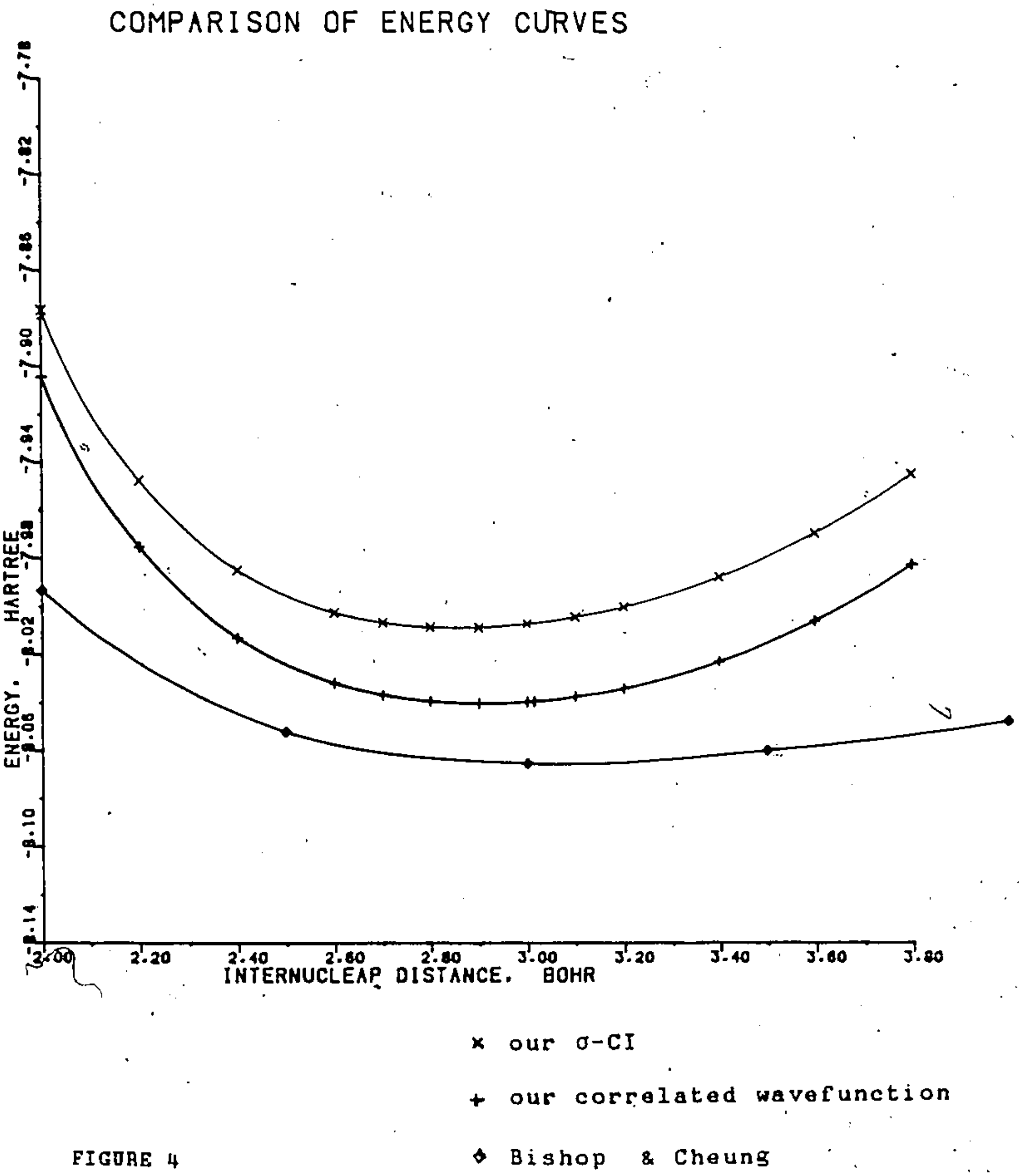
COMPARISON OF ENERGY CURVES
ENERGY, HARTREE
-7.78
-7.82
-7.86
-7.90
-7.94
-7.98
-8.02
-8.06
-8.10
-8.14
2.00
2.20
2.40
2.60
2.80
3.00
3.20
3.40
3.60
3.80
INTERNUCLEAR DISTANCE, BOHR
× our σ-CI
+ our correlated wavefunction
◆ Bishop & Cheung

FIGURE 4

have calculated, the correlation energy has been estimated[125] to be approximately constant with respect to internuclear distance, with the inner-shell correlation decreasing and the outer-shell correlation energy increasing. One might reasonably expect a small basis to better describe the cusps at short internuclear distances for reasons similar to those used for the more general wavefunction expansion, thereby decreasing the calculated internuclear distance, and making the energy improvement greater at short distances. Our results show otherwise. One can see from figure 5 that the energy improvement is greater for longer internuclear distances. The reason for this will be discussed in the section on interelectronic cusps.

By subtracting our lowest energy from the theoretical energies of the atoms, one can obtain an approximate potential relative to the dissociation limit, -0.0623 a.u., compared with the experimental[125a] -0.0924 a.u.

Dipole Moment

The dipole moment of the correlated wavefunction was

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[125] F. Moscardo, G. Delgado-Barrio, Int. J. Quantum Chem. 19, 1 (1981)

[125a] W. C. Stwalley, W. T. Zemke, K. R. Way, K. C. Li, T. D Proctor, J. Chem. Phys. 66, 5412 (1977)

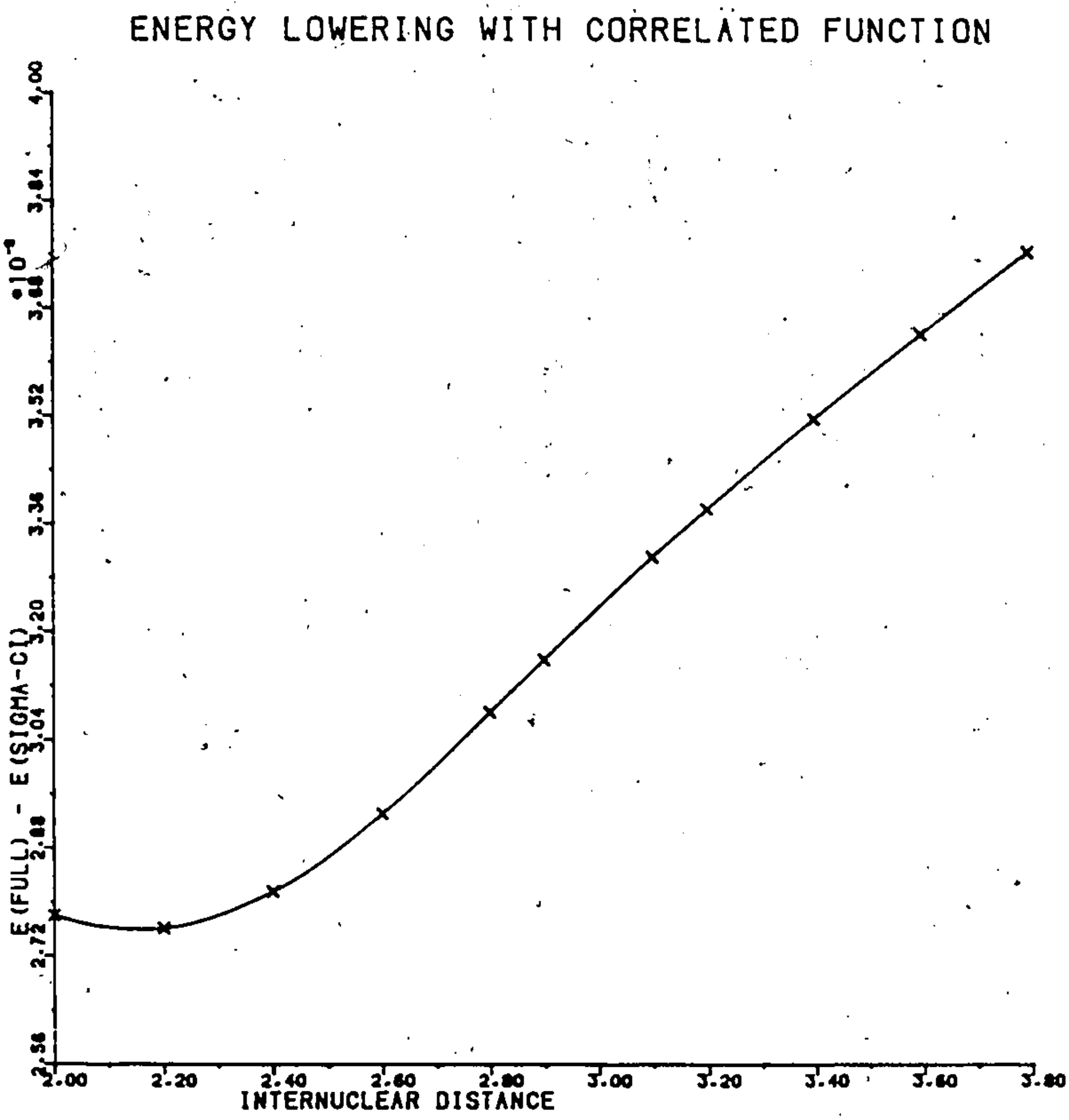
ENERGY LOWERING WITH CORRELATED FUNCTION
E(FULL) - E(SIGMA-CI)
*10^-2
4.00
3.84
3.68
3.52
3.36
3.20
3.04
2.88
2.72
2.56
2.00
2.20
2.40
2.60
2.80
3.00
3.20
3.40
3.60
3.80
INTERNUCLEAR DISTANCE

FIGURE 5

2.2721 a.u. at the internuclear distance of 3.015 bohr. The wavefunction without explicit correlation gives a similar dipole moment of 2.2732 at 3.00 bohr. The experimental dipole moment[126], calculated by extrapolating experimental data to a vibrational quantum number of -1/2, is 2.293 atomic units, while the best available Hartree-Fock calculation[127] is 2.36180 at an internuclear distance of 3.015 bohr.

The best available variational calculation of the dipole moment of LiH at R = 3.015 bohr is probably that of Roos and Sadlej[128]. Although their best CAS (complete active space) SCF results do not have the lowest available CI energy, it is made from a large polarized basis set designed for accurate calculations of electric moments. Their calculated dipole moment is 2.2921 a.u.

It is also possible to have a wavefunction that yields good values for the energy and poor ones for the dipole

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[126] L. Wharton, L.P. Gold, W. Klemperer, J. Chem. Phys. 37, 2149 (1962)

[127] L. Laaksonen, D. Sundholm, P. Pyykko, Chem. Phys. Lett. 94, 573 (1985)

[128] B.O. Roos and A.J. Sadlej, Chem. Physics 94, 43 (1985)

moment. The dipole moment of Clary's best correlated wavefunction of LiH, for example, was 2.392 a.u., worse even than a Hartree-Fock calculation.

The small change in the dipole moment with the addition of explicitly correlated functions is not very surprising if one reasons that the part of the correlation which most affects the value of the dipole moment is the "left-right" correlation, most of which is already present in a σ-CI calculation. One can see (figure 6) that the change in dipole moment is small at all internuclear distances. The value of

$$\left(\frac{\mu_e}{R_e}\right)/\left[\frac{\partial\mu}{\partial R}\right]_{R=R_e} ,$$

(equation 6)

can be calculated numerically from the three internuclear distances (2.9, 3.015, 3.1) to give the value 1.514 (experimental[129] 1.8±0.3)

The related value of the derivative of the dipole moment with respect to the internuclear distance has been reported experimentally[130] as ±0.42±0.06 atomic units, while

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[129] T.C. James, W.G. Norris, W. Klemperer, J. Chem. Phys. 32, 728 (1960)

[130] J. Gerratt and I.M. Mills, J. Chem. Phys. 49, 1719 (1968)

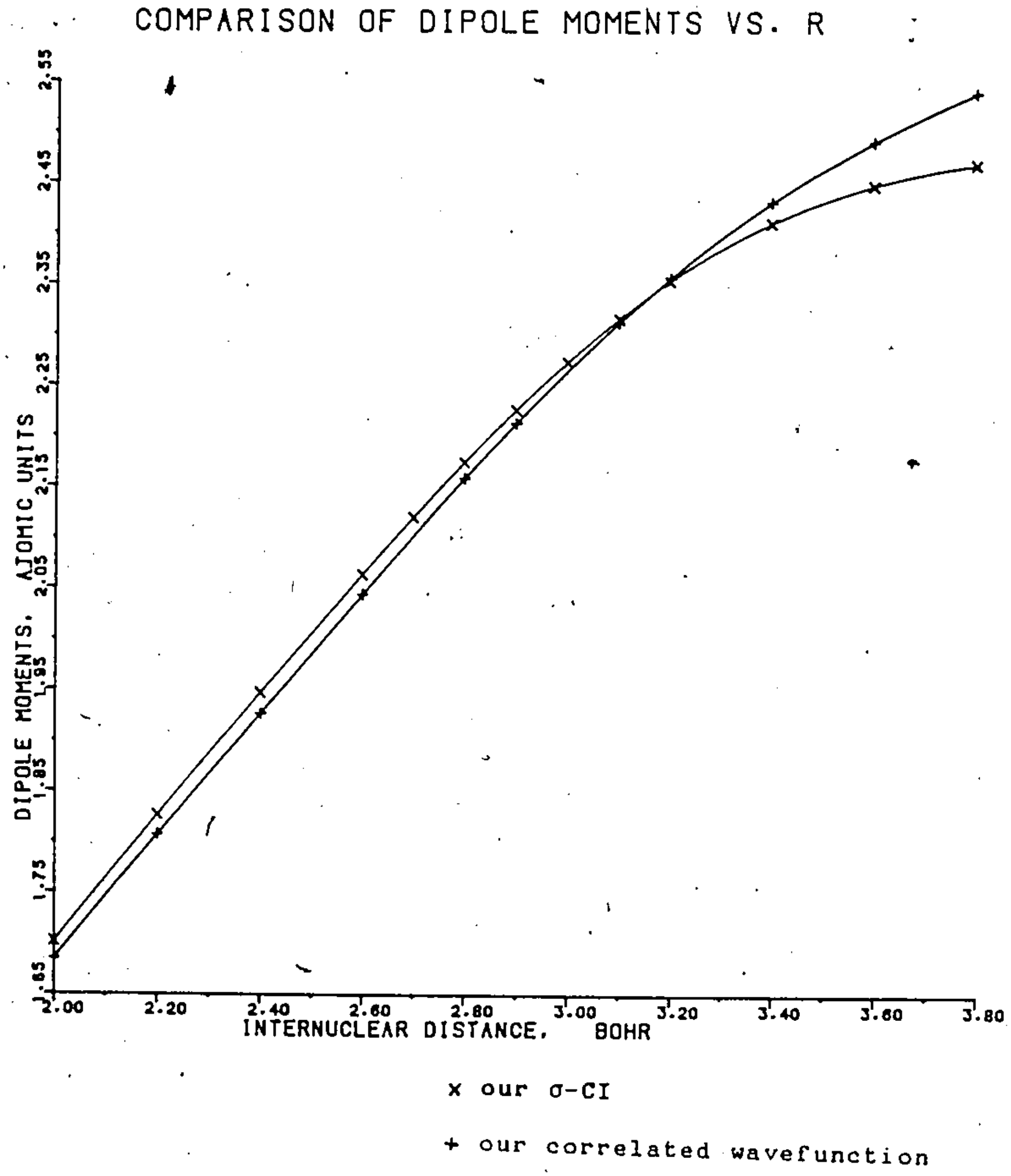
COMPARISON OF DIPOLE MOMENTS VS. R
DIPOLE MOMENTS, ATOMIC UNITS
1.65
1.75
1.85
1.95
2.05
2.15
2.25
2.35
2.45
2.55
2.00
2.20
2.40
2.60
2.80
3.00
3.20
3.40
3.60
3.80
INTERNUCLEAR DISTANCE, BOHR
× our σ-CI
+ our correlated wavefunction

FIGURE 6

our calculated value is 0.4979 atomic units. Another reference[131] gives an experimental value of 0.48 to this property. There is a large scatter in the published calculated values. Gready, Bacskay, and Hush[132] give a value of 0.486 for the SCF wavefunction and 0.373 for a CI calculation. Meyer and Rosmus[133] reported a value of 0.448 from a CEPA (correlated electron pair approximation) calculation.

Quadrupole Moment

The quadrupole moment, measured with the nuclear centre of mass of the ^{7}Li ^{1}H molecule as the origin, of the full wavefunction at R=3.015 is -3.1598 a.u. and -3.2198 at R=3.00 for the σ-CI wavefunction. Here again, the small change with explicit correlation can be explained with the reasoning that the important "left-right" and "in-out"

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[131] D. Steele and W.B. Person in "Molecular Spectroscopy, vol. 2, eds. R.F. Barrow et al. (Chemical Society Specialist Periodical Report, London, 1974)

[132] J.E. Gready, G.B. Bacskay, N.S. Hush, Chem. Phys. 24, 333 (1977)

[133] W. Meyer and P. Rosmus, J. Chem. Phys. 63, 2356 (1975)

correlation is already present in a σ-CI calculation. (See figure 7)

The best available quadrupole moments are again from Roos & Sadlej[138], with a value of -3.0699 a.u. at 3.015 bohr. The best numerical SCF quadrupole moment is that of Laaksonen et al.[133], with a value of -3.37006 a.u. at 3.015 bohr. The value of the quadrupole moment is a more sensitive test of the valence shell orbitals and of the valence correlation correction than the energy.

Other Properties

Among the other observables and expectation values that have been calculated, one can find $\langle x^2 \rangle = \langle y^2 \rangle$, $\langle z^2 \rangle$ measured from either the coordinate origin ($\langle z^2 \rangle$) or the center of mass ($\langle z^2 \rangle$), and $\langle r^2 \rangle$ measured from the coordinate origin or the two nuclei, and $\langle z \rangle$. They are compared with other published values in table VI.

The values of Bishop and Cheung[illegible] can be used as the benchmark for these properties. Most of our moments are consistently low. This result can be attributed to the insufficient expansion of the uncorrelated part of the

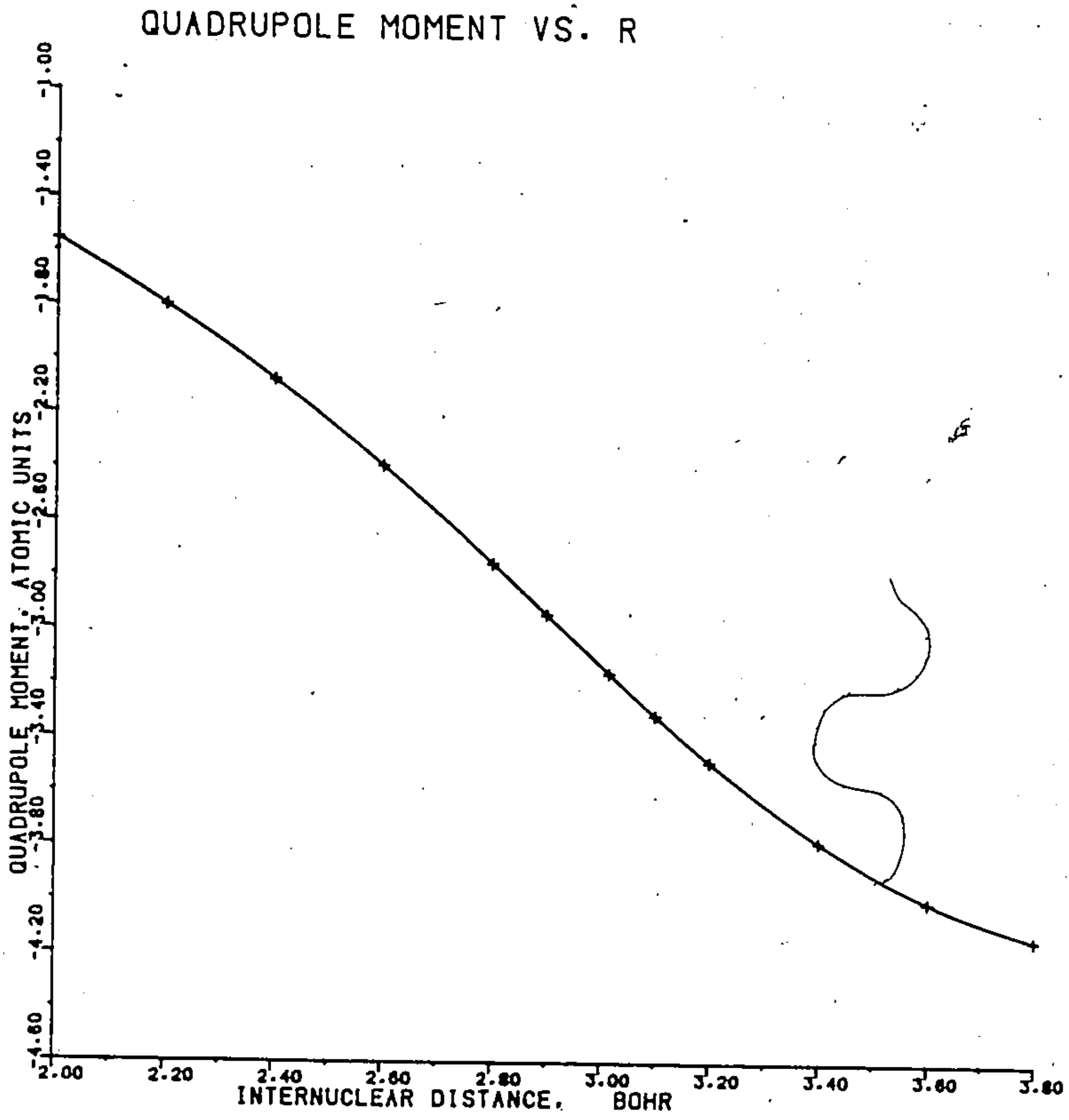
QUADRUPOLE MOMENT VS. R
QUADRUPOLE MOMENT, ATOMIC UNITS
-1.00
-1.40
-1.80
-2.20
-2.60
-3.00
-3.40
-3.80
-4.20
-4.60
2.00
2.20
2.40
2.60
2.80
3.00
3.20
3.40
3.60
3.80
INTERNUCLEAR DISTANCE, BOHR

FIGURE 7

TABLE VII

Comparison of observables

authors	ref.	$\langle x^2 \rangle$	$\langle z^2 \rangle_0$	$\langle z^2 \rangle_{cm}$	$\langle r^2 \rangle_0$	$\langle r_A^2 \rangle$	$\langle r_b^2 \rangle$	$\langle z \rangle_0$
Bender & Davidson	88	3.91	10.91		18.7			-0.67
Docken & Hinze	134	4.05	10.93		19.01	25.97	30.10	-0.69
SCF McCullough	101							-0.65
Melius & Goddard	135					26.8		
Bishop & Cheung	136		10.9127		18.89	25.74	30.03	-0.7146
This work		3.70	10.82	14.24	18.23	25.83	28.81	-0.74

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[134] K. K. Docken and J. Hinze, J. Chem. Phys. 57, 4936 (1972)

[135] C. F. Melius and W. A. Goddard III, J. Chem. Phys. 56, 3348 (1972)

[136] D. M. Bishop and L. M. Cheung, J. Chem. Phys. 79, 2945 (1983)

wavefunction as well as to the small number of nonlinear parameters, making the function less flexible far from the nuclei. It is possible for a wavefunction to give a good value for the energy, yet have poor values for the expectation values,[137] as was seen earlier in the case of dipole moments.

Other properties, including the Larmor term and the estimated upper bounds to the parallel and the perpendicular polarizabilities are listed in appendix 2 for various internuclear distances. The polarizability upper bounds are, as expected, rather high ($\alpha_\parallel \leq 154.42$; $\alpha_\perp \leq 43.22$, compared with[138] $\alpha_\parallel = 26.3$, $\alpha_\perp = 29.9$)

Polarizabilities

Polarizabilities and hyperpolarizabilities are difficult to calculate by variational methods for several reasons. First, the basis set of the wavefunction used must be large

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[137] H. M. James and A. S. Coolidge, Phys. Rev. 51, 860 (1937)

[138] B. O. Roos and A. J. Sadlej, J. Chem. Phys. 76, 5444 (1982)

enough and flexible enough to give similarly accurate eigenfunctions to the original Hamiltonian and to the Hamiltonian perturbed by an electric field. Second, the eigenfunctions must be calculated to sufficient accuracy to make the differencing between similar values numerically accurate. Third, since the perturbed eigenvalue is an infinite expansion in the field strength whose coefficients are only defined at the origin, care must be taken to extrapolate finite-field calculations to zero field or to eliminate the effects of the higher hyperpolarizabilities. If the wavefunction does not obey the Hellmann-Feynman theorem, there is a further problem of discrepancy between polarizability tensor elements obtained from the variation of the energy with field and those from the variation of the dipole moment.

The basis set problems are difficult to solve by variational methods. Of course, if the basis set has no projection onto the point group of the perturbed system, the calculated tensor elements will be zero, but with a more general basis set, there is no guarantee that the calculated values will be accurate.

The second and third problems can be lessened by the use of Richardson's extrapolation as described in the previous chapter. Errors due to higher polarizabilities can be eliminated order by order until convergence, as can numerical errors that depend on the field. Random numerical error, although not corrected, can be detected since it prevents convergence. If random errors exist at some field strength, the calculation can be repeated with different fields. The extrapolation also allows comparable values to be calculated from energies and multipole moments and compared.

Our value for the first electric polarizability in the z direction (α_{zz})is 14.59 a.u. (compare with 26.3 as mentioned in the previous section). This value is very low, probably because of the lack of flexibility of the basis set. Using five fields was sufficient to achieve convergence to at least four figures in this value, derived from either the dipole or energy, and agreement between the two to at least 6 figures.

The value of the ß polarizability in the z direction is not as well known. The estimates of it in an SCF description range from -200.67 a.u.[139] to -733.16 a.u.[140] , with the most likely values those of Lazzeretti[141] , with a value of -310.562, or of Bishop and

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[139] G.P. Arrighini, J. Tomasi, G. Petrongolo, Theoret. Chim. Acta <u>18</u> , 341 (1970)

[140] J.M. O'Hare and R.P. Hurst, J. Chem. Phys. <u>46</u> , 2356 (1967)

[141] P. Lazzeretti, E. Rossi, R.Zanasi, J. Phys. B. <u>15</u>,

Lam[142] , with one of -309. Bishop and Lam in the same paper report an MCSCF (multi-configuration self-consistent field) value of -686. Our value, converged to four digits and with three-digit agreement between dipole moment and energy calculations, is β_{zzz}=-235. It should be pointed out that our expressions for the "odd" polarizabilities such as β do not depend on the accuracy of the "even" polarizabilities such as α.

Interorbital cusps

The purpose of explicitly correlated wavefunctions is to accurately describe the wavefunction in the neighbourhood of the interelectronic cusps. The derivatives of the exact solution of the Schroedinger equation with respect to the interelectronic distances at the electronic cusps are 1/2.[143] The second derivatives at the same points should be 1/6. [76] In the absence of any angular coordinates in

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521 (1982)

[142] D. M Bishop and B. Lam, Chem. Phys. Lett. <u>120</u> , 69 (1985)

[143] W. Kolos and C. C. J. Roothaan Rev. Mod. Phys. <u>32</u> , 205 (1960)

the uncorrelated part of the wavefunction, the interelectronic distances are independent coordinates and their derivatives are easily evaluated. While they can be evaluated at any point in Euclidian space, we have chosen to use an average integrated over the wavefunction. Presumably, the variational theorem will make the derivative closer to its theoretical value in the regions of high electronic density, where it will result in a greater drop in total energy, and further (most likely closer to zero) elsewhere.

By including only some classes of the explicitly correlated configurations in the wavefunction, one can study what is the effect of each of these types of terms on the energy as well as on the derivatives of the interelectronic cusps, and therefore get a better idea as to what types of terms are most important to include in an explicitly correlated wavefunction.

The values labelled in table VII as D12 and S12 are defined as

$$D12 = \int \phi \, [\partial \phi / \partial r_{12}]_{r_{12}=0} \, d\tau$$

$$S12 = (1/2) \int \phi \, [\partial^2 \phi / \partial r_{12}{}^2]_{r_{12}=0} \, d\tau$$

(equation 7)

as was discussed in chapter 6. The behaviour of the wavefunction in the neighbourhood of the cusp can be expected[73] to look like figure 8. A first order approximation to this behaviour, using only the first power of the interelectronic coordinates, can be expected to underestimate the slope, or first derivative, at the cusps. A function including only the second power of these coordinates will have a positive rather than a negative second derivative.

Table VII compares the energies and cusp derivatives of several variational wavefunctions, most of them defined by excluding a class of configurations from the full explicitly correlated wavefunction. These classes are: all configurations with the second power of an interelectronic distance; all those with the first power; all those with a nonzero power of r_{34}; all those with a power of r_{12}; all those involving the third nonlinear parameter. All but the one with only one spin function are for an internuclear distance of 3.015 bohr. The constrained wavefunction will be defined in a later section.

WAVEFUNCTION NEAR THE CUSP

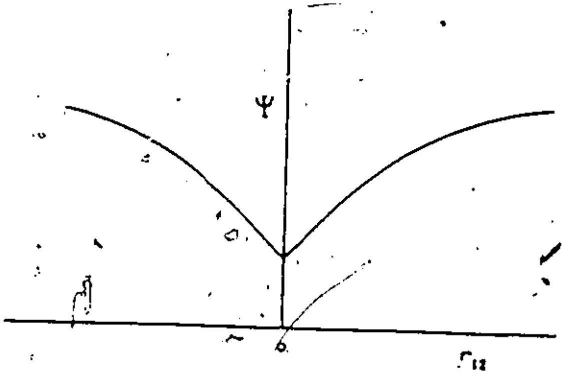


FIGURE 8

TABLE VII

Energies and cusp derivatives

function	E	E-E(CI)	E(full)-E	D12	S12	D34	S34
theoretical				0.5	0.0833	0.5	0.0833
full	-8.03946		0	0.3762	-0.0748	0.2506	-0.0299
σ-CI	-8.0073	0		-	-	-	-
no r_{ab}^{2}	-8.0303	0.0230	0.00915	0.2475		0.1088	
no r_{ab}^{1}	-8.0221	0.0148	0.0174		0.1805		0.0139
no r_{34}^{n}	-8.0293	0.0220	0.0102	0.2685	0.0117		
no r_{12}^{n}	-8.0140	0.0067	0.0255			0.1633	-0.0144
no 3rd para.	-8.0350		0.0015	0.3692	-0.0686	0.2394	-0.0268
1 spin	-8.0350		0.0045	0.3651	-0.0694	0.2439	-0.0296
constrained	-8.0295		0.0099	0.35	-0.050	0.21	-0.024

The cusp derivatives behave more or less as predicted when the first or second powers of the interelectronic distance are excluded from the wavefunction. The sum of the individual contributions to the lowering of the energy due to the first power alone or to the the second power alone is greater than the energy lowering due to both classes of terms together The two types of terms can therefore compensate in part for each other. It is, in fact, possible to represent most of the correlation by the use of only even powers of the interelectronic coordinates, as it is possible to use only odd powers. Although the correlation energy retrieved by the first power of the interelectronic coordinates is the greater part of the correlation, the contribution from the second power is still important both to the lowering of the energy and to the improvement of the cusp derivatives.

On the other hand, the sum of the individual energy contributions of the inner-shell and the outer-shell configurations (r_{12} and r_{34} respectively,) is smaller than their combined effect. Partitioning correlation energy into "inner" and "outer" shell angular correlation is therefore difficult. The arguments of James and Coolidge[20] concerning the need for correction to the uncorrelated part of the wavefunction far from the interelectronic cusp may be used to account for this. It may be that when the outer shell is explicitly correlated, that part of the wavefunction which had previously been engaged in cusp-fitting would then have more flexibility to describe the electronic distribution far from the inner-shell interelectronic cusp, and vice-versa. The worsened value of the cusp derivatives of the "one-shell-correlated" functions tend to bear this out.

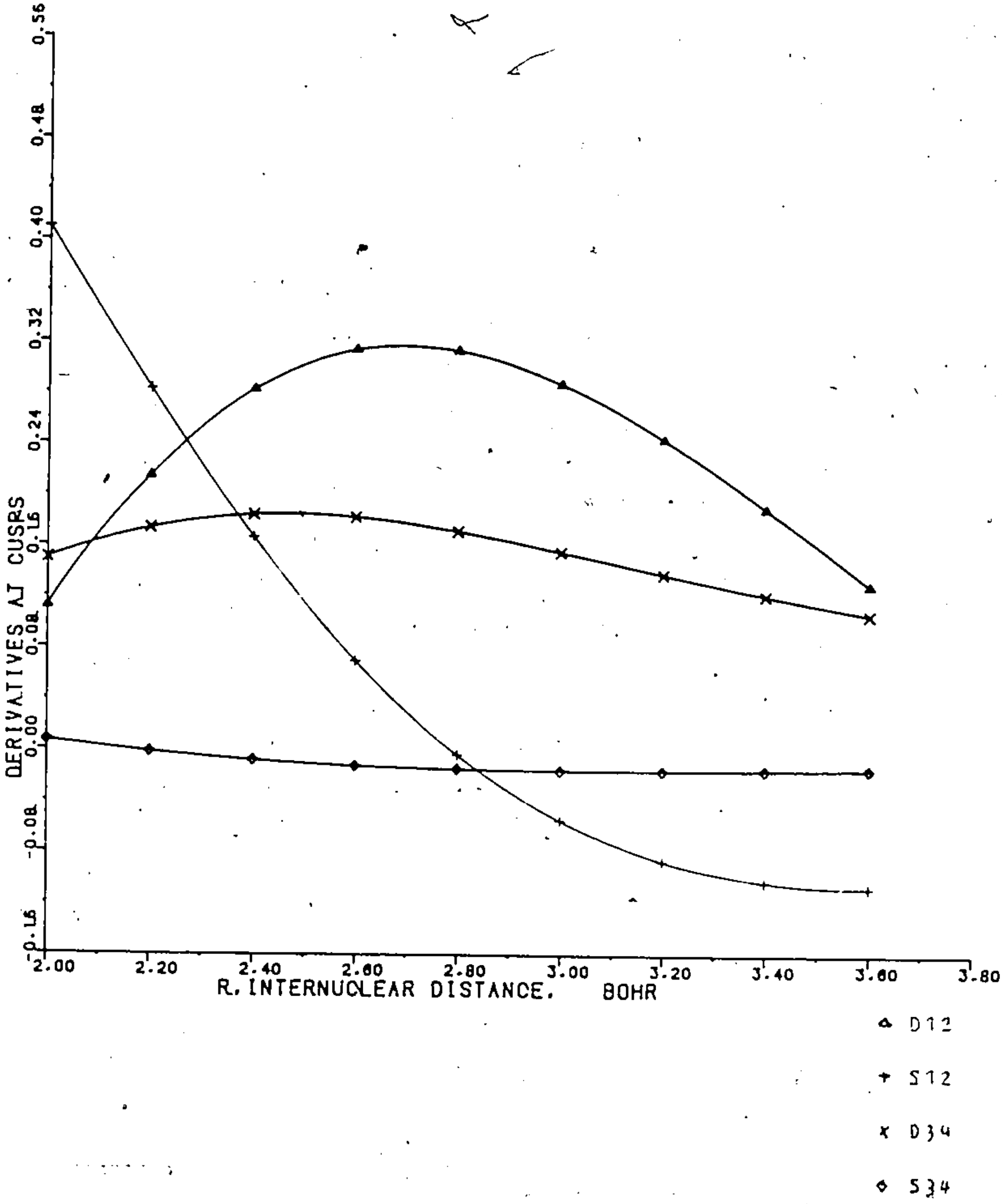
If we attempt to separate the inner-shell and the outer-shell angular correlation by adding inner-shell correlating terms to a σ-CI wavefunction, and then add to that wavefunction the outer-shell correlating terms, and record the energy lowering at both steps, we can compare these.

values with those of other authors (see table V). This leads to the tentative conclusion that our correlated wavefunction had recovered most of the inner-shell angular correlation and not quite enough of the outer-shell angular correlation.

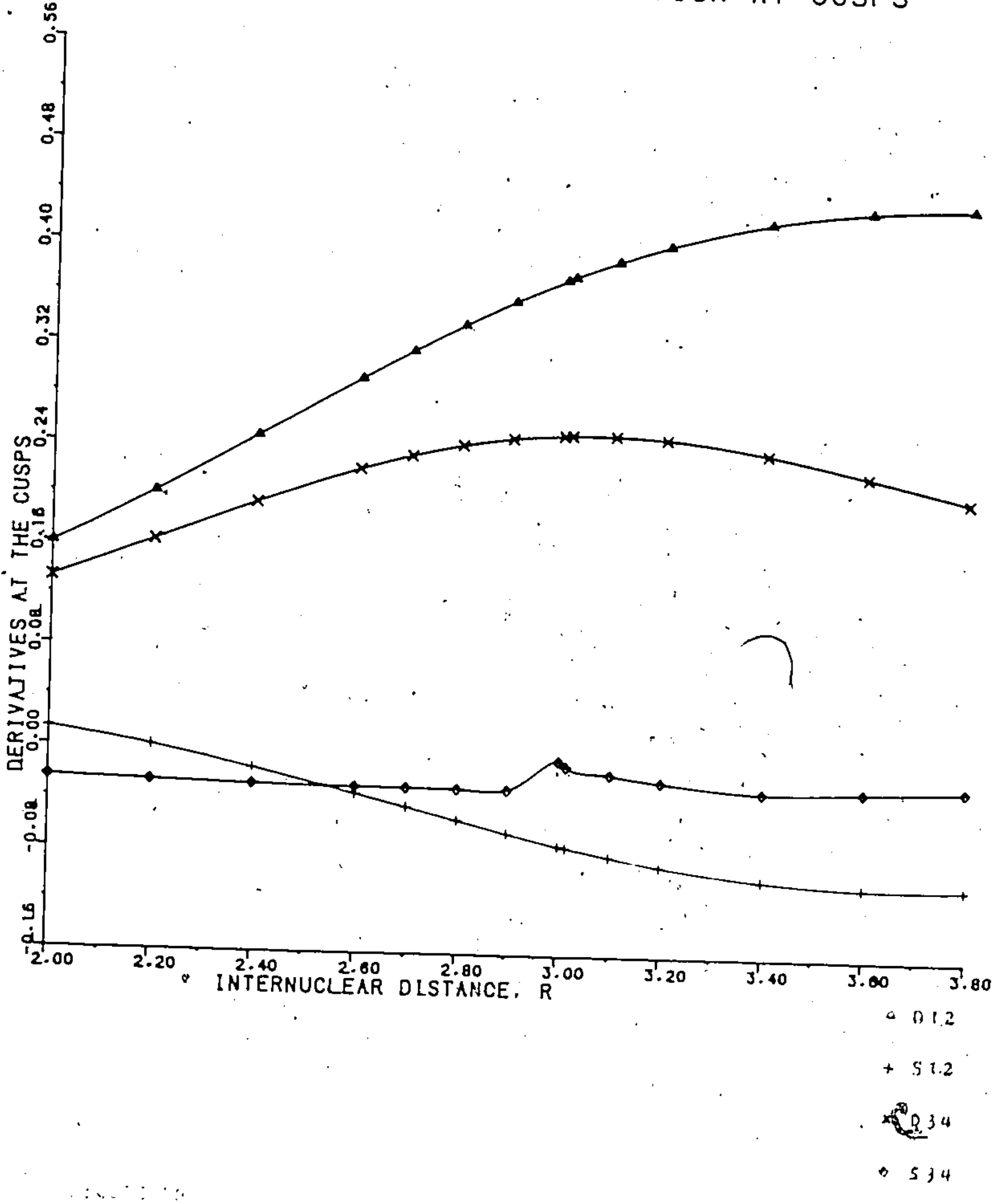
The cusp derivatives and their variation with internuclear distance give a very clear picture of the effect of different types of James-Coolidge functions on the correlation. Remembering that almost all the configurations multiplied by a power of the interelectronic distance in our wavefunction had all j=0, we plotted the cusp derivatives vs. R for a correlated wavefunction where all j=0 in all configurations, correlated or not. This plot, figure 9, shows not only low values for the first derivatives at the cusps, but derivatives that are very dependent on R.

However, when the uncorrelated part of the basis set is expanded to include powers of ξ, the cusps derivatives are not only greatly improved near the equilibrium internuclear distance (figure 10), but becomes much less dependent on the distance. In fact, the cusp derivative of the inner shell interaction increases with internuclear distance. This dependence of the cusp derivative on distance closely parallels the unexpected improvement in correlation energy recovered with increasing internuclear distance. It therefore seems that not only does the correlation provided

BEHAVIOUR AT CUSPS, ALL J=0



BEHAVIOUR OF THE WAVEFUNCTION AT CUSPS



by explicitly correlated configurations depend acutely on the flexibility of the rest of the wavefunction in ε, but the optimal nonlinear parameters for such configurations may differ considerably from the optimal nonlinear parameters of uncorrelated configurations.

Restricted Hartree-Fock approximation

It is possible to constrain the full so-called σ-CI wavefunction so that it approximates a single-determinant single-spin-function wavefunction. If the two space orbitals of such a single-determinant 4-electron wavefunction can be expressed as:

$$\Psi = A\,[\Phi'_1(1)\,\Phi'_1(2)\,\Phi'_3(3)\,\Phi'_3(4)]$$

(equation 9)

then the single configuration can be expanded as:

$$\Phi'_1(a) = \sum_{n=1}^{N} C_{1,n}\Phi_n(a) \quad ; \; C_{1,n} = C_{2,n} \; ; \; C_{3,n} = C_{4,n}$$

(equation 10)

The set of M basis functions can be partitioned into two sets, according to the value of the nonlinear parameter. One set of N functions will be used to form the first Φ' orbital only, and the other M-N functions will be used for the second Φ' orbital only:

$$\Phi'_3(c) = \sum_{n=N+1}^{M} C_{3,n}\Phi_n(c)$$

(equation 11)

The constrained wavefunction can therefore be expanded as:

$$\psi = \Big(\sum_{k>l}\sum\Big)\Big(\sum_{m>n}\sum\Big) K_{klmn}\, A\,[\Phi_k(1)\Phi_l(2)\Phi_m(3)\Phi_n(4)]$$

$$K_{klmn} = C_{1,k}\, C_{2,l}\, C_{3,m}\, C_{4,n}\, [2-\delta(k,l)][2-\delta(m,n)]$$

(equation 12)

Such an approximation to a single-configuration wavefunction can therefore be obtained using terms from our wavefunction, by restricting the linear parameters to the coefficients shown above. Of course, not all terms are available, and we must assume that the ones not included would have had a negligible effect on the energy. Each of the orbital expansion coefficients is varied until the energy reaches a minimum. This minimum is not necessarily an upper bound to the Hartree-Fock energy if all of the terms are not present, since it comes from a multi-determinant rather than a single-determinant function.

The optimal coefficients were obtained by a crude method. Each coefficient was varied individually, using a parabolic interpolation, to minimize the energy. The lowest energy obtained by this method was -7.9587 hartree, compared with the SCF energy of -7.98735 hartree[133] or a difference of 0.0286 hartree.

Constrained wavefunction

When the wavefunction is constrained to the form

$$\psi_c = \psi(a + br_{12} + cr_{12}^2 + dr_{34} + er_{34}^2) \qquad \text{(equation 13)}$$

the constrained energies and derivatives seem to converge to the wavefunction shown in table VIII. Over two thirds of the correlation energy is kept, relative to our full wavefunction, even with such an approximation to a constrained function of a very restricted form. The cusp derivatives are almost as good as in the original full wavefunction. This seems to indicate that this type of function, while effective at representing the cusps, may not be quite flexible enough away from it.

TABLE VIII
CUSP DERIVATIVES

	Variational	Constrained
D12	0.376	0.35
S12	-0.0798	-0.050
D34	0.251	0.21
S34	-0.0299	-0.024

Split shell and second spin function

It is to be noted that configurations involving the second power of the intershell interelectronic distances were tested, with very little effect on the energy. No configurations involving the first power of such coordinates were included because of this. Clary had the same experience with this molecule.

Removing all configurations involving the third nonlinear parameter has remarkably little effect on the energy. The effect of these terms may have been reduced by the rather long expansion with $j = 0$ (powers of ξ) in the wavefunction, as well as the fact that linear dependence problems precluded the the presence of many such terms.

Although the effect on the cusp derivatives is small, it is marginally greater for the outer shell.

Elimination of the second spin function had a slightly greater effect on the energy, and a similar effect on the cusp derivatives. Here, the effect was greater on the inner shell. The second spin function allows for greater interaction between the inner and the outer shells. For this reason, it probably contributes to correcting the orbitals far from the interelectronic cusps.

Linear dependence

The large number of correlated configurations, the large number of configurations of other types, and the fact that the matrix elements involving three interelectronic distances can only be evaluated with limited accuracy all have contributed to making linear dependence an important problem in this study. Because of this, many of the basis functions which caused significant lowering of the energy in a smaller basis set had to be discarded from larger calculations to avoid the problem of linear dependence.

Wavefunctions suffering from linear dependence can be identified by abnormally lowered variational energy and greater dipole moments, and by the large linear coefficients and energy contributions of a group of related configurations. If the overlap matrix is diagonalized, the lowest eigenvalue of such a matrix is small, and the linear coefficient of the corresponding function in this transformed basis for the variational wavefunction will be large.

It is possible to reduce linear dependence by removing from a basis transformed to the eigenfunctions of the overlap matrix that eigenfunction which has the smallest eigenvalue. This, however, makes the wavefunction's properties more difficult to calculate and to interpret, since some of the operators may not be as simple in the transformed basis. An alternative is to simply remove from the configuration set some of those that are the leading terms in the lowest overlap eigenfunctions. This is easily done and, in the same way as before, will increase the value of the lowest eigenvalue of the overlap matrix. In this way, it is more likely that those matrix elements whose inaccuracy is at the root of the linear dependence will be removed from the matrix altogether.

Although in a case of linear dependence there is a choice to be made as to which configurations will be deleted, it seemed that linear dependence could be reduced most effectively by removing some terms of two types: terms having a third nonlinear parameter, and terms having the first power of r_{34}. By removing a combination of five or six such functions, linear dependence was reduced to a level comparable to that of a small σ-CI calculation. It was also because of apprehended linear dependence that terms multiplying the third nonlinear parameter by ξ_3 or ξ_3^2 were not included in the wavefunction.

What these results may point to is a need for greater accuracy in evaluating the many-electron integrals involving small nonlinear parameters, especially when the configuration set is large. It is unfortunate that terms containing the third nonlinear parameter were added to a matrix where most of the multielectron integrals had already been evaluated. The linear dependence problem was not discovered until both types of functions were used. Recalculating the values of only a few selected matrix elements with greater accuracy, rather than all of them, did not improve the linear dependence very much.

It is worth noting that the energy contribution of the explicit correlation of the outer shell seems to be small compared to Ebbing's[80] estimate for nonangular correlation, and that a large number of explicitly correlated terms containing r_{34} had to be rejected due to the negligible energy lowering caused by including terms containing $r_{34}{}^2$. These two effects might have been caused by the lack of accuracy in evaluating integrals involving small nonlinear parameters. It may well be, however, following the arguments of James and Coolidge,[20] that the energy lowering due to the explicit correlation in the outer shell depends on the presence in the configuration set of terms having smaller nonlinear parameters, even if those terms may not be important in an uncorrelated calculation.

CHAPTER 8

CONCLUSIONS

The present work shows that it is possible to build an explicitly correlated wavefunction for multielectron diatomics with few restrictions. The use of this type of wavefunction has been restricted in the past as to the form of the correlated configurations by the difficulty in calculating the Hamiltonian matrix elements between explicitly correlated configurations. This has prevented the development until now of wavefunctions flexible enough to give values of observables besides electronic energy.

The choice of basis sets has been made to balance the ease of evaluation of the matrix elements and the flexibility of the set with the speed of convergence of the configurations. Interpretation of the results must be made from this perspective. The relatively good values for the dipole moment show the importance of a flexible basis set in the calculation of observables. Other moments and observables have been calculated with an accuracy which, although not nearly as good as those obtainable from other types of wavefunctions, could not have been contemplated with more restricted explicitly correlated wavefunctions. The behaviour of the wavefunction near the interelectronic cusp could not even have been studied without such a flexible explicitly correlated wavefunction. The present basis set does not converge quickly enough to give useful potential energy curves, but the same method could be used with a more appropriate basis set.

Our experience with the behaviour of explicitly correlated multielectron wavefunctions in a very flexible basis set can easily be used to make more rapidly convergent wavefunctions of this type. Since the time-consuming portion of the calculation was due not to the difficulty in evaluating the multielectron integrals but rather to the number of such integrals, one can expect a more rapidly convergent expansion to have a major effect on the computational effort involved in such a calculation.

Such a rapidly convergent wavefunction can probably be attained by the following five steps. First, a small σ-CI expansion can be built from an appropriate basis set and tranformed to Brueckner[98] or natural orbitals, or approximations to them. These orbitals will be most efficient at representing the one-electron distribution of a correlated function. Most of the so-called correlation corrections to one-electron expectation values comes not from the correlation but from the improved first-order density function. Most of the correction can be achieved by replacing Hartree-Fock orbitals by Brueckner or natural orbitals[144] Second, the leading term or terms of a σ-CI expansion in terms of these orbitals can be multiplied by the first and second powers of the interelectronic distances. Third, the one-electron distribution can be corrected with a more extensive σ-CI calculation if recalculation of the Brueckner orbitals shows that they have shifted significantly since the addition of the explicit correlation. Fourth, the linearity in $\vec{r}$ at large distances from the nuclei caused by the explicit correlation can be

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[144] S. Larsson and R. E. Brown, Int. J. Quantum Chem. 12 , 83 (1977)

removed by adding, variationally, configurations that are linear in $\vec{r}$ at long distances.

As a fifth step, for high accuracy, radial-radial and radial-angular multielectron correlation can be introduced without the use of coupled correlated terms by multiplying "excited" configurations by powers of the interelectronic distances.

Since most of the computational difficulties in evaluating very flexible explicitly correlated wavefunctions for multielectron diatomics have been addressed, it is hoped that very low energies can soon be achieved, without compromising the other properties, in larger molecules.

APPENDIX 1

Atomic Units

The units in all reported results and all equations in this thesis are, unless otherwise indicated, atomic units. These units do not all have common names. Their equivalents in SI units[145] are given below.

units of	name	SI equivalent
energy	hartree	4.3594×10^{-18} J
length	bohr	5.2916×10^{-11} m
dipole moment		8.4778×10^{-30} C m
electric field		5.1422×10^{11} V m^{-1}
quadrupole moment		4.4866×10^{-40} C m^2
α polarizability		1.6488×10^{-41} C^2 m^2 J^{-1}
β polarizability		3.2063×10^{-53} C^3 m^3 J^{-2}

The SI equivalents of these atomic units is dependent on the accuracy of the measurement of the fundamental constants.

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[145] R. McWeeny, B.T. Sutcliffe, "Methods of Molecular Quantum Mechanics", Academic Press, New York, 1976; D.M. Bishop and G. Maroulis, J. Chem. Phys. 82, 2380 (1985)

APPENDIX 2

The following tables presents the values of some of the properties and expectation values of three different wavefunctions at different internuclear distances. The first table gives values for the full correlated wavefunction, the second one for the σ-CI wavefunction, and the third one for the full wavefunction without the second spin function. The first column is the internuclear distance, the second is the expectation value $\langle z \rangle$, summed over all electrons and taking the centre of mass as the origin; the third gives the expectation value $\langle z^2 \rangle$ with the origin at the nuclear midpoint and the fourth the same expectation value measured from the centre of mass; the fifth column gives the expectation value of the operator $\langle x^2+y^2 \rangle$; the next column gives the expectation value of the operator $\langle r^2 \rangle$ from the nuclear midpoint; the next two give the expectation value of the same operator measured from the two nuclei; the following column is the Larmor term defined in Chapter 6; and the next two are the estimated upper bound to the parallel and perpendicular polarizabilities defined in the same chapter. All these properties are given in atomic units except for the Larmor term, which is in units of 10^{-6} erg G^2 $mole^{-1}$.

```
  R    <Z>CM     <Z2>    <Z2>CM <X2+Y2>  <R2>    <RA2>   <RB2>    LARMOR    A|| <    A+ <
2.000 -2.6800  5.5096  7.2805 4.9528 10.4625 15.0927 13.8323  -8.2075  66.2024 25.1677
2.200 -2.9019  6.4916  8.5584 5.6518 12.1434 17.7689 16.1980  -9.4952  80.5030 29.4707
2.400 -3.1205  7.4975  9.8759 6.2425 13.7400 20.4472 18.5528 -10.7042  96.0558 33.4253
2.600 -3.3376  8.5309 11.2386 6.7094 15.2403 23.1124 20.8882 -11.8252 113.0464 36.9169
2.800 -3.5516  9.6049 12.6556 7.0708 16.6757 25.7988 23.2326 -12.8809 131.8077 40.0095
2.900 -3.6560 10.1622 13.3859 7.2282 17.3905 27.1744 24.4265 -13.3992 141.9789 41.4889
3.100 -3.8551 11.3278 14.8883 7.5436 18.8715 30.0563 26.9067 -14.4549 164.1744 44.583
3.200 -3.9486 11.9396 15.6597 7.7211 19.6607 31.5878 28.2135 -15.0074 176.3111 46.3182
3.400 -4.1232 13.2271 17.2430 8.1537 21.3809 34.8779 31.0039 -16.1905 202.9472 50.4313
3.600 -4.2830 14.6035 18.8826 8.7201 23.3236 38.5001 34.0672 -17.4992 233.1075 55.6610
3.800 -4.4313 16.0673 20.5798 9.4344 25.5017 42.4607 37.4227 -18.9405 267.2360 62.2120
******************************************
************* SIGMA-CI ********************
******************************************
2.000 -2.6963  5.5233  7.3185 4.8917 10.4150 15.0127 13.8174  -8.1778  66.3971 24.8573
2.200 -2.9206  6.5308  8.6285 5.6225 12.1534 17.7414 16.2454  -9.5145  81.0368 29.3180
2.400 -3.1406  7.5756  9.9900 6.2764 13.8521 20.5193 18.7049 -10.8077  97.1243 33.6069
2.600 -3.3568  8.6529 11.3979 6.8213 15.4743 23.3081 21.1605 -12.0271 114.7490 37.5323
2.700 -3.4630  9.2035 12.1174 7.0481 16.2516 24.7025 22.3808 -12.6042 124.1815 39.3231
2.800 -3.5672  9.7623 12.8457 7.2474 17.0098 26.1017 23.5978 -13.1611 134.0602 41.0087
2.900 -3.6685 10.3305 13.5814 7.4256 17.7562 27.5151 24.8174 -13.7024 144.4182 42.6223
3.000 -3.7659 10.9097 14.3231 7.5926 18.5023 28.9560 26.0487 -14.2352 155.2974 44.2172
3.100 -3.8583 11.5017 15.0698 7.7599 19.2617 30.4399 27.3034 -14.7680 166.7486 45.8609
3.200 -3.9453 12.1090 15.8210 7.9389 20.0479 31.9818 28.5940 -15.3095 178.8289 47.6249
3.400 -4.1022 13.3765 17.3387 8.3702 21.7467 35.2858 31.3276 -16.4475 205.1188 51.7700
3.600 -4.2389 14.7224 18.8827 8.9387 23.6612 38.9259 34.3165 -17.6876 234.6406 57.0565
3.800 -4.3597 16.1488 20.4578 9.6637 25.8125 42.9146 37.5904 -19.0399 267.8357 63.7244
******************************************
************* 1 SPIN FUNCTION *************
******************************************
2.000 -2.6731  5.4487  7.2092 4.8543 10.3031 14.9471 13.6590  -8.0777  65.4536 24.6673
2.200 -2.8966  6.4380  8.4960 5.5572 11.9952 17.6313 16.0391  -9.3745  79.8203 28.9774
2.400 -3.1186  7.4637  9.8386 6.1710 13.6347 20.3458 18.4436 -10.6193  95.6133 33.0423
2.600 -3.3408  8.5235 11.2374 6.6657 15.1893 23.0550 20.8435 -11.7876 112.9598 36.6764
2.800 -3.5618  9.6233 12.6953 7.0462 16.6695 25.7723 23.2467 -12.8862 132.1077 39.8702
3.000 -3.7757 10.7760 14.2115 7.3678 18.1439 28.5780 25.7098 -13.9624 153.4229 42.9078
3.200 -3.9746 11.9970 15.7793 7.7157 19.7128 31.5881 28.3175 -15.0827 177.3338 46.2862
3.400 -4.1541 13.2970 17.3915 8.1624 21.4595 34.8947 31.1442 -16.2993 204.2685 50.4850
3.600 -4.3151 14.6799 19.0456 8.7463 23.4263 38.5385 34.2341 -17.6361 234.6394 55.8285
```

APPENDIX 3

The space part of the configurations can be represented by the expression:

$$\left(\prod_{k=1}^{4} P_{l_k}^{m_k}(\eta_k)(x_k^2-1)^{|m_k|/2}\,\xi_k^{j_k}\,e^{-a_k\xi_k}\,e^{im_k\phi_k}\right) r_p^n \qquad \text{(equation 1)}$$

Each configuration can be represented by a series of 14 numbers:

$$l_1\ m_1\ j_1\ l_2\ m_2\ j_2\ l_3\ m_3\ j_3\ l_4\ m_4\ j_4\ p\ n \qquad \text{(equation 2)}$$

The interelectronic distance represented by r_p comes from the following table:

r_p :	p=	1	2	3	4	5	6	0
r_{ab}:	ab=	12	13	14	23	24	34	none

(equation 3)

The complete basis set used in this work is listed below.

20010000000000
10000000000000
20010010000000
10000010000000
20000000000000
20000010000000
10010000000000
30010000000000
10010010000000
30010010000000
30000000000000
30020000000000
30000010000000
00000000000000

30020010000000
20020000000000
00000010000000
20020010000000
20010020000000
10000020000000
40010000000000
40010010000000
20000020000000
40000000000000
40020000000000
40000010000000
10010020000000
40020010000000

30010020000000
30000020000000
30020020000000
30030000000000
50010000000000
40030000000000
00000020000000
20020020000000
30030010000000
50010010000000
40030010000000
50000000000000
20010000000011
20010010000011

10000000000011
10010000000011
00000000000011
20010000000012
10010000000012
10010010000012
20000000000011
10010010000011
10000010000011
30010000000011
20000010000011
20020000000011
30020000000011
30000000000011

```
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10000010000062   60000010000000   00100010000100   20010010100000
10010000000062   00000030000000   20010100000000   20010020100000
10000010000061   20020030000000   20000100000000   20010010110000
10000000000061   50000020000000   10100000000000   40110010000000
10010000000061   60020010000000   10000100000000   40100000000000
20000010000062   40040000000000   10000000100000   10000110000000
20000010000061   50020020000000   20120000000000   30020110000000
30010000000061   40010010010000   20020000100000   30010100000000
30000010000061   40040010000000   20100010000000   30030110000000
00000010000062   40010030000000   20000110000000   30000110000000
10000020000062   50040000000000   20000010100000   30010000100000
00000010000061   40000010010000   20000010000100   30000010100000
20010000000061   50040010000000   20100110000000   30010110000000
40010000000062   40020010010000   20110010000000   30020000100000
40010000000061   40000030000000   20010010000100   20000005000000
30010000000012   60030000000000   30120000000000   10000005000000
20110100000062   40020030000000   30110000000000   20020005000000
20000000000061   30020020010000   20200010000000   20000015000000
30010000000062   70010000000000   20000210000000   20000010005000
30000010000062   60030010000000   40110000000000   20010015000000
10000020000061   50030020000000   40010000100000   20010010005000
20110100000061   20020020010000   20120010000000   10010005000000
30010010000012   70010010000000   20020010000100   10000015000000
30000010000012   70000000000000   20210000000000   10000010005000
30020010000012   10110010000000   20010200000000   30020005000000
00000010000012   20110100000000   10010000200000   00000005000000
20020010000012   30000210000000   10010000100100   30000005000000
40010000000012   30210000000000   10000020100000   30010005000000
20010000000022   30310000000000   10000010100000   40010005000000
20010000000042   30010100100000   70000010000000   40020005000000
50020000000000   30110010000000   30030010010000   20020015000000
40010020000000   00100010100000   20020000000000   20020010005000
50000010000000   10110300000000   50010010010000   20010005000000
20010010010000   10210200000000   40030010010000   10010015000000
10000010010000   10210300000000   30030030000000   10010010005000
20010030000000   20110000000000   50010030000000   30010015000000
10000030000000   10000010200000   40030030000000   30010010005000
40000020000000   10200100000000   50000010010000   30000015000000
20000010010000   10110100000000   50020010010000   30000010005000
40020020000000   20010000100000   50000030000000   30020015000000
20000030000000   10010000100000   60040000000000   30020010005000
10010010010000   30110000100000   20110200000000   40000005000000
30010010010000   30100010100000   20200100000000   50010005000000
10010030000000   30000000100000   20100200000000   00000015000000
50030000000000   20210100000000   10100200000000   00000010005000
60010000000000   30200010000000   20200000000000   20010110000000
30010030000000   30300010000000   20000200000000   10100010000000
50030010000000   10010010000100   10200000000000   20000000100000
60010010000000   10110010000100   20010000100100   30010010100000
30000010010000   30210000100000   10000000100100   30010010000100
30030020000000   30110000200000   20200110000000   10010010100000
30020010010000   20210200000000   10200110000000   30100000000000
60000000000000   10110000000000   20000010100100   30000110000000
50010020000000   10210000000000   10000010100100   30100010000000
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10000020000000   10110000100000   20210110000000   00100000000000
30000030000000   20020010100100   10210110000000   00000000100000
40030020000000   10100210000000   20020000100100   30120010000000
30020030000000   10000010000100   20010010100100   30020010100000
00000010010000   60000010100000   300. 0000100100
20020010010000   30000010000100   00000000100100
```

```
30020010000100    30010010100100    30030005000000    30020000000061
20020010100000    30200000000000    20010015010000    20020000000061
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00000010000100    30200100000000    40000015000000    40020100000000
40010100000000    30220000000000    40000010005000    40020000100000
40010110000000    30020200000000    40020015000000    30130000000000
40010010100000    30000010100100    40020010005000    30030000100000
40010010000100    00200000000000    10000000000012    50110000000000
40000100000000    30220010000000    10000000000062    50010100000000
40000000100000    30020210000000    20010010000012    50010000100000
20010210000000    30020010100100    10000010000012    70020010000000
20210010000000    00200010000000    20000000000012    10010025000000
10000210000000    00000010100100    20000000000062    20010025000000
20100210000000    20220010000000    20000010000012    20010005100000
30010200000000    40210000000000    10010010000062    10000005100000
30010000100100    40010200000000    30000000000012    20010015100000
10210010000000    40200000000000    30020000000012    10000015100000
10010010100100    40000200000000    00000000000012
30210010000000    10000025000000    20010010000061
30010210000000    10000020005000    10010010000061
```