CORRELATION ENERGY OF TWO-ELECTRON SYSTEMS[*]

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ABSTRACT

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Correlated closed-shell and open-shell functions (due to Roothaan and Weiss) are analyzed in terms of a $1/Z$ expansion to obtain the corresponding first order wave functions and the second order energy. The need for expanding the open-shell functions in powers of $Z^{-\frac{1}{2}}$ is demonstrated. The contributions to the second order energy from radial and angular correlation are estimated.

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I. Introduction

In discussing the energy of the helium isoelectronic sequence, it is instructive to develop it in a series in inverse powers of the nuclear charge Z , viz.,

$$E = Z^2 E_0 + Z E_1 + E_2 + Z^{-1} E_3 + \ldots \ldots \tag{1}$$

The very accurate variation-perturbation calculations of Scherr and Knight[1], according to Hylleraas' method[2], provide the energy coefficients through the thirteenth order. These combined with Linderberg's[3] $1/Z$ analysis of the Hartree-Fock (H-F) energies permit an elucidation of the correlation energy[4] (E(corr)) in terms of the $1/Z$ series. We concentrate our attention on the leading term, $E_2(\text{corr}) = E_2(\text{exact}) - E_2(\text{H-F})$, and compare the efficacy with which selected functions reproduce this term.

Correlation may be introduced into a wave function in a number of ways[4]. These include the explicit introduction of an interelectronic coordinate, r_{12} or θ_{12}, and configuration interaction (C.I.), or a combination of the two. As a by-product of their perturbation calculations, Scherr and Knight[5] obtained the values of E_2 (Eq. (1)) corresponding to a C.I. function combined with the Legendre functions $P_\ell (\cos\theta_{12})$ for $\ell = 0,1,2$. By a variational treatment, Roothaan and Weiss[6] obtained closed- and open-shell wave functions containing terms in r_{12} for several members of the He sequence. We analyze the R-W functions in terms of a $1/Z$ expansion. From the first order functions, both E_2 and E_3 may be obtained. For E_3, numerical inconsistencies, discussed in the appendix, precluded detailed analysis. However, for E_2 it proved possible to calculate the separate contributions from the R-W orbital and correlation functions. This enabled

1. C. W. Scherr and R. E. Knight, Rev. Mod. Phys. 35, 436 (1963).

2. E. A. Hylleraas, Z. Physik 65, 2091 (1930).

3. J. Linderberg, Phys. Rev. 121, 816 (1961).

4. P. O. Löwdin, Advances in Chemical Physics II, New York, 1959, p.207.

5. C. W. Scherr and R. E. Knight, J. Chem. Phys. 40, 1777 (1964).

6. C. C. J. Roothaan and A. W. Weiss, Rev. Mod. Phys. 32, 194 (1960). Hereafter, we refer to this work as R-W.

us to estimate the amounts of radial and angular correlation energy
included in E_2 for their functions. It is in these terms that we
compare in Table I the R-W functions with the others mentioned above.

In order to establish our notation, the necessary formalism of
the 1/Z perturbation expansion is set down in Section II, and the
results are discussed in the final section.

II. 1/Z Expansion of Correlated Functions

It is convenient to make the transformation

$$r_i = Z^{-1} \rho_i \; ; \; r_{ij} = Z^{-1} \rho_{ij} \qquad (2)$$

which scales the unit of length[7] by the nuclear charge Z . Thus, the
non-relativistic Schrödinger equation becomes[8]

$$(H_0 + Z^{-1} H_1) \Psi(Z) = Z^{-2} E(Z) \Psi(Z) .$$

For the He sequence,

$$H_0 = -\tfrac{1}{2} (\nabla_1^2 + \nabla_2^2) - (\rho_1^{-1} + \rho_2^{-1})$$

is the hydrogenic Hamiltonian for two electrons and

$$H_1 = \rho_{12}^{-1}$$

is the interelectronic potential. The wave functions for the ^{1}S
ground states of these two electron systems factor into an anti-
symmetric spin function and a symmetric function of the spatial
coordinates of the electrons. Since we are using a spin-free
Hamiltonian, the spin function is left out of further consideration.

We follow the usual Rayleigh-Schrödinger perturbation develop-
ment in expanding E(Z) and Ψ(Z) in powers of the perturbation
parameter 1/Z . Thus, we write

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7. The unit of length is Za_o and the unit of energy is 1 Hartree =
   e^2/a_o throughout this paper.

8. The notation F(Z) is used to indicate the Z dependence of
   various quantities explicitly. Those not so marked are indepen-
   dent of Z .

$$\Psi(Z) = \sum_n \Psi_n \, Z^{-n} \quad , \quad E(Z) = \sum_n E_n \, Z^{2-n} \quad . \tag{3}$$

With the normalization chosen to be

$$\langle \Psi(Z) \mid \Psi(Z) \rangle = \langle \Psi_0 \mid \Psi_0 \rangle = 1 \, , \tag{4}$$

The following relations are readily derived[9]:

$$\Psi_0 = \pi^{-1} \exp(-\rho_1 - \rho_2) \, , \tag{5}$$

$$\langle \Psi_0 \mid \Psi_1 \rangle = 0 \, , \tag{6}$$

$$E_0 = \langle \Psi_0 \mid H_0 \mid \Psi_0 \rangle = -1, \quad E_1 = \langle \Psi_0 \mid H_1 \mid \Psi_0 \rangle = 5/8, \tag{7}$$

$$E_2 = \langle \Psi_0 \mid H_1 - E_1 \mid \Psi_1 \rangle \, , \quad \text{etc.}$$

The R-W correlated functions are of the form

$$\Psi(Z) = \phi(Z, \rho_1, \rho_2) \, \chi(Z, \rho_{12}). \tag{8}$$

We impose the additional normalization condition

$$\langle \phi(Z) \mid \phi(Z) \rangle = 1, \tag{9}$$

and expand $\phi(Z)$ and $\chi(Z)$ in powers of Z^{-1} ,

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9. See, for example, the discussion of perturbation techniques by J. O. Hirschfelder, W. Byers Brown, and S. T. Epstein, Advances in Quantum Chemistry I, 1964, Academic Press, New York.

$$\emptyset(Z) = \sum_m z^{-m} \emptyset_m (\rho_1, \rho_2) , \tag{10}$$

$$\chi(z) = \sum_n z^{-n} \chi_n (\rho_{12}) . \tag{11}$$

For these expansions to be consistent with that given in Eq. (3), it follows that

$$\Psi_0 = \emptyset_0 \chi_0 , \tag{12}$$

$$\Psi_1 = \emptyset_0 \chi_1 + \emptyset_1 \chi_0 , \tag{13}$$

and so forth. Eq. (5) then fixes χ_0 and $\emptyset_0$ to be

$$\chi_0 = 1 , \emptyset_0 = \pi^{-1} \exp(-\rho_1 - \rho_2) . \tag{14}$$

Eq. (6) becomes

$$\langle \emptyset_0 | \emptyset_0 \chi_1 \rangle + \langle \emptyset_0 | \emptyset_1 \rangle = 0 . \tag{15}$$

Because of the normalization chosen for $\emptyset(Z)$, Eqs. (6) and (9), each term in Eq. (15) is separately zero. Substituting from Eqs. (12), (13) and (14) into Eq. (7) we find

$$E_2 = \langle \emptyset_0 | H_1 - E_1 | \emptyset_0 \chi_1 \rangle + \langle \emptyset_0 | H_1 - E_1 | \emptyset_1 \rangle \tag{16}$$

$$= E_2(\chi_1) + E_2(\emptyset_1) .$$

To calculate these separate contributions to E_2 we need to find χ_1 and $\emptyset_1$.

We deal first with $\chi(z, \rho_{12})$ of Eq. (8). Since the R-W correlation functions for various Z are power series in r_{12}, we may write Eq. (11) in the form

$$\chi(z, \rho_{12}) = \sum_{n=0} z^{-n} \chi_n = \sum_{n=0} z^{-n} \sum_{m=0} \gamma_{nm} \rho_{12}^m , \tag{17}$$

where, according to Eq. (14), $\gamma_{00} = 1$, $\gamma_{0m} = 0$, $m > 0$. For $n > 0$, the γ_{nm}, and in particular the γ_{1m} which define χ_1, were obtained by the least squares analysis described in the appendix.

The R-W orbital functions (ϕ of Eq. (8)) are of the form

$$\phi(z, \rho_1, \rho_2) = \varphi(z, \rho_1)\psi(z, \rho_2) + \psi(z, \rho_1)\varphi(z, \rho_2) \qquad (18)$$

where, for the closed-shell case $\varphi \equiv \psi$. The analysis is slightly less straight forward than that for the correlation function. It turns out that, for the open-shell function, the individual ϕ_m of Eq. (10) are given correctly, not be expanding the one electron functions $\varphi(z)$ and $\psi(z)$ separately in powers of z^{-1}, but rather[10] in powers of $z^{-\frac{1}{2}}$. This is most readily demonstrated by introducing the functions[11]

$$u(z, \rho_j) = 2^{-\frac{1}{2}}\left[\varphi(z, \rho_j) + \psi(z, \rho_j)\right] , \qquad (19\text{-a})$$

$$v(z, \rho_j) = 2^{-\frac{1}{2}}\left[\varphi(z, \rho_j) - \psi(z, \rho_j)\right] \qquad (19\text{-b})$$

where the $\varphi(z, \rho_j)$ and $\psi(z, \rho_j)$ are normalized to satisfy Eq. (9).

The orbital function may be rewritten in terms of u and v,

$$\phi(z, \rho_1, \rho_2) = u(z, \rho_1)u(z, \rho_2) - v(z, \rho_1)v(z, \rho_2) . \qquad (20)$$

Thus, the open-shell function may be put in the form of a super-position of two closed-shell functions. Since the R-W functions were obtained by a variational procedure, the Z-independent term of their orbital functions is exactly ϕ_0 given by Eq. (14) (to the numerical accuracy of their calculations). It follows that the Z-independent term of uu is ϕ_0 and that of vv is identically zero.

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10. W. Byers Brown, University of Wisconsin Theoretical Chemistry Institute Report TCI-49.

11. See, for example, C. A. Coulson and I. Fischer, Phil. Mag. 40, 386 (1949); Sir Lennard-Jones and J. A. Pople, Phil. Mag. 43, 581 (1952).

Since, according to Eq. (10), $\emptyset(Z)$ admits only integral powers of Z^{-1}, the expansions for $u(Z)$ and $v(Z)$ must be

$$u(Z) = \sum_{n=0} Z^{-n} u_n , \quad v(Z) = \sum_{n=0} Z^{-(n+\frac{1}{2})} v_{n+\frac{1}{2}} . \tag{21}$$

Substituting these expansions into Eqs.(19), we find

$$\varphi(Z) = 2^{-\frac{1}{2}} \left[u(Z) + v(Z) \right] = 2^{-\frac{1}{2}} \left[u_0 + Z^{-\frac{1}{2}} v_{\frac{1}{2}} + Z^{-1} u_1 + \ldots \right] ,$$

$$\psi(Z) = 2^{-\frac{1}{2}} \left[u(Z) - v(Z) \right] = 2^{-\frac{1}{2}} \left[u_0 - Z^{-\frac{1}{2}} v_{\frac{1}{2}} + Z^{-1} u_1 - \ldots \right] .$$

In the special case of the closed-shell functions $\varphi(Z) \equiv \psi(Z)$ and therefore $v(Z) \equiv 0$.

The comparison of Eq. (18) with Eq. (9) shows that

$$\emptyset_0 = u_0(\rho_1) u_0(\rho_2)$$

$$\emptyset_1 = u_0(\rho_1) u_1(\rho_2) + u_1(\rho_1) u_0(\rho_2) - v_{\frac{1}{2}}(\rho_1) v_{\frac{1}{2}}(\rho_2) . \tag{22}$$

The functions u_1 and $v_{\frac{1}{2}}$ were obtained by a least squares analysis of Eq. (21), as described in the appendix.

III. Results and Discussion

The last column in Table I lists the values of E_2 for a few selected functions, and also the values of $E_2(\chi_1)$ and $E_2(\emptyset_1)$ calculated according to Eq. (16). For the R-W functions we also obtained E_2 by a least squares analysis of the total energies. The values of E_2 so obtained agree with the sums $E_2(\emptyset_1) + E_2(\chi_1)$ to at least one in the fourth decimal place. This allows us to make some quantitative deductions.

It is apparent from the data collected in Table I that $E_2(\text{corr}) = -0.0466$ a.u. We may further subdivide $E_2(\text{corr})$ into contributions from radial and angular correlations[11,12].

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12. G. R. Taylor and R. G. Parr, Proc. Nat. Acad. Sci. (U. S.) 38, 154 (1952).

With the help of E_2 for the radial limit function,[3,13] which we assume contains all of E_2(rad), we obtain for the exact function E_2(rad) = -0.0143 a.u. and E_2(ang) 6 -0.0324 a.u. For the C. I. functions involving Legendre polynomials of $\cos\theta_{12}$, such as analysis of E_2 follows directly from the calculations of Scherr and Knight[5].

For the R-W functions we estimate the radial and angular contributions to E_2, shown in Table I, by means of the following arguments. We first note that for their closed-shell function $E_2(\emptyset_1)$ can contribute only to E_2(H-F); the remainder (-0.0460 a.u.) of E_2(H-F) must come from $E_2(\chi_1)$[14]. The remaining part of $E_2(\chi_1)$ for the closed-shell, namely -0.0440 a.u., must be attributed to correlation effects, both radial and angular.

We now assume that for the open-shell function $E_2(\emptyset_1)$ and $E_2(\chi_1)$ make the same contribution to E_2(H-F) as they do in the closed-shell case, namely -0.0650 a.u. and -0.0460 a.u., respectively. Certainly the R-W open-shell function describes radial correlation better than the R-W closed-shell function. Since the correlation functions are of the same form in the two cases, we expect them both to describe angular correlation about equally well. Therefore, we assume that the difference of -0.0022 a.u. between the total E_2(open) and E_2(closed) gives precisely the difference between E_2(rad) for the functions. Clearly, the difference $E_2(\emptyset_1)_{open} - E_2(\emptyset_1)_{closed}$ = -0.0068 a.u. is also due entirely to radial correlation. At this point we have only to account for the discrepancy of 0.0005 a.u. between the exact E_2 and that obtained for the R-W open-shell function. We have arbitrarily assigned 0.0003 a.u. of the discrepancy to the angular part and 0.0002 a.u. to the radial part of E_2(corr). Thus, a little arithmetic enables us to estimate the radial and angular contributions to E_2(corr) for both R-W functions.

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13. H. L. Davis, J. Chem. Phys. 39, 1827 (1963).

14. Although one expects some contribution to E_2(H-F) from $\chi(r_{12})$, its magnitude is somewhat surprising. This serves to emphasize the importance of optimizing the orbital and correlation functions together in a variational calculation.

It is evident from Table I that an open-shell treatment is essential to describe radial correlation fully since even the correlated closed-shell function cannot do so. Angular correlation is introduced more efficiently by powers of r_{12} than by Legendre polynomials $P_{\ell}(\cos\theta_{12})$. Clearly, the terms of r_{12}^2 and r_{12}^4 are equivalent to $\ell = 1$ and $\ell = 1,2$ functions, respectively. The odd powers r_{12} and r_{12}^3 introduce higher order Legendre polynomials whose contributions are not negligible. To a large extent the success of the R-W functions may be attributed to the inclusion of these odd powers of r_{12}.

Table I. Approximate Contributions to E_2 from the 'Independent Motion' of the Electrons, and from Radial and Angular Correlations.[a]

Wave Function	E_2(H-F) Independent Motion	E_2(radial) Radial Correlation	E_2(angular) Angular Correlation	E_2 Total
1. Closed-shell - Hartree-Fock[b]	0.1110	0.0	0.0	0.1110
2. Open-shell - Legendre Expansion,[c]				
$\ell = 0$	0.1110	0.0143	0.0	0.1253
$\ell = 0 + \ell = 1$	0.1110	0.0143	0.0264	0.1518
$\ell = 0, + \ell = 1, + \ell = 2$	0.1110	0.0143	0.0301	0.1554
3. Correlated closed-shell[d]				
$E_2(\phi_1)$	0.0650	0.0	0.0	0.0650
$E_2(\chi_1)$	0.0460	0.0119	0.0321	0.0901
Total	0.1110	0.0119	0.0321	0.1550
Least squares total	------	------	------	0.1551
4. Correlated open-shell[d]				
$E_2(\phi_1)$	0.0650	0.0068	0.0	0.0718
$E_2(\chi_1)$	0.0460	0.0073	0.0321	0.0854
Total	0.1110	0.0141	0.0321	0.1572
Least squares total	------	------	------	0.1572
5. Exact[e]	0.1110	0.0143	0.0324	0.1577

a. All energies in $-e^2/a_0$.

b. Reference 3.

c. Reference 5.

d. This work; analysis of functions given in Reference 6.

e. Reference 1.

Acknowledgements

IV. Appendix

In unnormalized form, which we indicate by subscript u, the R-W functions are[6]

$$\Psi_u(Z, r_1, r_2, r_{12}) = \chi_u(Z, r_{12}) \, \phi_u(Z, r_1, r_2)$$

$$\chi_u(Z, r_{12}) = \sum_{k=0}^{4} c_k \, \zeta^k r_{12}^{\;k}$$

$$\phi_u(Z, r_1, r_2) = \varphi_u(Z, r_1) \, \psi_u(Z, r_2) + \psi_u(Z, r_1) \, \varphi_u(Z, r_2) \qquad \text{(A-1)}$$

$$\varphi_u(Z, r_j) = \exp{-(\zeta r_j)} \sum_{k=0}^{4} a_k \, \zeta^k r_j^{\;k}$$

$$\psi_u(Z, r_j) = \exp{(-\zeta r_j)} \sum_{k=0}^{4} b_k \, \zeta^k r_j^{\;k}$$

In these equations a_k, b_k, c_k and ζ are all functions of Z.[15] For the closed-shell of course, $a_k = b_k$ and $\phi_u = \varphi_u \, \varphi_u$.

The least squares analyses therefore all involve the solution of an over determined set of equations of the form

$$D(Z, y) = \sum_{n=0}^{N} Z^{-n} \sum_{m=0}^{M} d_{nm} y^m \qquad \text{(A-2)}$$

with $y = \rho_j$ or ρ_{12}, and the coefficients d_{nm} are to be determined. The function $D(Z,y)$ is known for $Z = 1,2,3,4,6,8,10$ and for a range of values of y.

After scaling according to Eq. (2) and normalizing to satisfy Eqs. (4) and (9) we obtain, for the correlation function

$$D(Z, \rho_{12}) = \sum_{k=0}^{4} \gamma_k(Z) \, \rho_{12}^{\;k} \qquad \text{(A-3)}$$

where $\gamma_k(Z) = (\zeta/Z)^k \, c_k(Z) \left[\langle \phi_u(Z) \mid \phi_u(Z) \rangle / \langle \Psi_u(Z) \mid \Psi_u(Z) \rangle \right]^{\frac{1}{2}}$

$$\text{(A-4)}$$

The right hand side of Eq. (A-1) is then equivalent to

$$\sum_{n=0}^{N} Z^{-n} \chi_n = \sum_{n=0}^{N} Z^{-n} \sum_{m=0}^{4} \gamma_{nm} \, \rho_{12}^{\;m}. \qquad \text{(A-5)}$$

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15. We used the values obtained from the R-W computer output rather than the rounded numbers given in ref. 6, with improved results.

As noted in the text, $\gamma_{0m} = \delta_{0m}$ where δ_{0m} is the Kronecker delta. There are two sources of inconsistency among the input data $D(Z, \rho_{12})$ calculated for given Z and ρ_{12}. Firstly, Roothaan and Weiss carried out the optimization to different degrees of accuracy for different Z. Secondly, they used the same expansion length up to $k = 4$ in Eqs. (A-1) and (A-3) for all Z despite the fact that correlation effects are relatively more important for small Z than for large Z. We set $M = 4$, in Eq. (A-2), corresponding to $k_{max} = 4$ in Eq. (A-3). To test the sensitivity of the γ_{nm} (in particular γ_{1m}) of Eq. (A-5) to these inconsistencies, least squares analyses[16] were carried out using different values of N in Eq. (A-2) and varying the range of ρ_{12} over which the function $D(Z, \rho_{12})$ was evaluated. We used in all combinations the ranges of $\rho_{12} = 0.1$-2.0, 0.1-3.0, 0.1-4.0 Za_0 and the expansion lengths $N = 3,4,5$. Larger values of N were not practicable since the equations (A-2) rapidly approached degeneracy as N increased. This is due to the fact that, for the Z values used, the quantities $\sum_k Z_k^{-n}$ which arise in the analysis rapidly approach a constant value as N is increased.

As a test of the quality of our analysis the $\chi_1(\rho_{12})$ which we extracted were used to calculate the integral $\langle \phi_0 \phi_0 \chi_1 \rangle$, which should be zero according to Eqs. (6) and (15). As is seen from Table A-1, this integral is sensitive both to the range of ρ_{12} used and the expansion length N. The results of the best case, $0.1 \leq \rho_{12} \leq 2.0$ and $N = 4$, suggests that the χ_1 obtained are accurate to about four decimal places. We further tested the consistency of the R-W correlation functions by relaxing the constraint $\gamma_{0m} = \delta_{0m}$. For $0.1 \leq \rho_{12} \leq 2.0$ and $N = 4$ we obtained from a new least squares analysis $\gamma_{00} = 1.0004$ (instead of exactly 1) and all γ_{0m}, $m \geq 1$, less than 4×10^{-4} in magnitude. It seems safe to assume, therefore, that the γ_{1m} listed in Table A-2 represent χ_1 of the R-W correlation function to about four decimal places. The integrals $E_2(\chi_1) = \langle \phi_0 | H_1 - E_1 | \phi_0 \chi_1 \rangle$ are also probably accurate, in the best case, to about four decimal places.

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16. J. B. Scarborough, Numerical Mathematical Analysis, (Johns Hopkins Press, Baltimore, 1950) Art. 113.

For the orbital functions $u(Z, \rho_j)$ and $v(Z, \rho_j)$ given by Eqs. (19) and (21) the least squares analyses were essentially the same as for the correlation functions. Now,

$$D(Z, \rho_j) = \pi^{\frac{1}{2}} \exp\left[(1 - \xi/Z) \rho_j \right] \sum_{k=0}^{4} (\alpha_k + \beta_k) \rho_j^k \quad \text{(A-8)}$$

for $u(Z, \rho_j)$, and

$$D(Z, \rho_j) = (2\pi)^{\frac{1}{2}} \exp\left[(1 - \xi/Z)\rho_j\right] \sum_{k=0}^{4} (\alpha_k - \beta_k)\rho_j^k \quad \text{(A-9)}$$

for $v(Z, \rho_j)$. The α_k and β_k in these two equations are related to the a_k and b_k of Eq. (A-1) by

$$\alpha_k(Z) = 2^{-\frac{1}{2}}(\xi/Z)^k a_k(Z) \left[\left\langle \phi_u(Z, \rho_1, \rho_2) \middle| \phi_u(Z, \rho_1, \rho_2) \right\rangle\right]^{-\frac{1}{4}}$$

and similarly for β_k with a_k replaced by b_k. The form of Eqs. (A-8) and (A-9) was chosen so that in Eq. (21)

$$u_n = \exp(-\rho_j) \sum_{m=0}^{M} \alpha_{nm} \rho_j^m \quad \text{(A-10)}$$

$$v_{n+\frac{1}{2}} = \exp(-\rho_j) \sum_{m=0}^{M} \beta_{nm} \rho_j^m \quad \text{(A-11)}$$

with $\alpha_{0m} = \delta_{0m}$, according to Eq. (14). As in the analyses for the correlation function, we set $M = 4$ in Eq. (A-2). In this case, however, an error is thereby introduced since the exponential in $D(Z, \rho_j)$ yields non-vanishing terms in r_j^5 and higher powers. We estimated the term in r_j^5 to be at least ten times smaller than that in r_j^4. We expect that the neglect of terms r_j^n, $n \geq 5$, introduced errors no larger than the others inherent in our treatment.

According to Eqs. (4) and (9) the integral $\left\langle \phi_0 \middle| \phi_1 \right\rangle = 0$ for an exact treatment. We used the value of this integral to select the optimum range of ρ_j and expansion length N over which to fit the orbital functions. Typical results are given in Table A-II where we also list the corresponding values of $E_2(\phi)$. In addition, Table A-II shows the importance of the terms $v_{\frac{1}{2}} v_{\frac{1}{2}}$, Eq. (22), in recovering all of ϕ_1, for the open-shell function. For the closed-shell, of course, $v_{\frac{1}{2}} = 0$.

The best set of expansion coefficients $\alpha_{1m}, \beta_{1m}, \gamma_{1m}$ which define χ_1 and ϕ_1, Eqs. (A-5), (A-10), (A-11) and (22),are listed in Table A-III. There we also list the coefficients of a Laguerre expansion of ϕ_1, for the R-W closed-shell function and compare them with the coefficients of the Laguerre expansion of ϕ_1 for the H-F function reported by Linderberg[3]. It is apparent that ϕ_1 for the R-W and H-F functions are considerably different. This serves to illustrate the significant change in an orbital function when it is made part of a correlated function.

Because of the errors in ϕ_1 and χ_1 the sum $E_2 = E_2(\phi_1) + E_2(\chi_1)$ may be less certain than the values of the individual terms. We checked these calculations with a least squares analysis of $\left[E(Z) - (-Z^2 + 5Z/8)\right]$ where the $E(Z)$ are the total energies reported by R-W for various Z [15]. The values of E_2 listed in Table I and labeled least squares correspond to an analysis including terms up to Z^{-3}. It was not possible to obtain reliable results by including higher order terms because of the difficulties caused by near degeneracy, as discussed above.

Table A-I. Integrals Involving χ_1 for Typical Least Squares Analyses.

N	Range of ρ_{12}	Closed-Shell		Open-Shell	
		$\langle \phi_0 \phi_0 \chi_1 \rangle$	$E_2(\chi_1)$	$\langle \phi_0 \phi_0 \chi_1 \rangle$	$E_2(\chi_1)$
3	0.1-2.0	-0.00176	-0.09002	-0.00243	-0.08530
3	0.1-3.0	-0.00173	-0.09003	-0.00242	-0.08531
3	0.1-4.0	-0.00173	-0.09003	-0.00242	-0.08531
4	0.1-2.0	+0.00001	-0.09006	+0.00046	-0.08544
4	0.1-3.0	+0.00044	-0.09024	+0.00076	-0.08556
4	0.1-4.0	+0.00043	-0.09023	+0.00075	-0.08556
5	0.1-2.0	-0.01019	-0.08619	+0.00130	-0.08594
5	0.1-3.0	-0.00450	-0.08842	+0.00199	-0.08628

Table A-II. Integrals Involving ϕ_1 for Typical Least Squares Analyses.

N	Range of ρ_i	Closed-Shell		Open-Shell neglecting terms in $v_{\frac{1}{2}} v_{\frac{1}{2}}$		Open-Shell including terms in $v_{\frac{1}{2}} v_{\frac{1}{2}}$	
		$\langle \phi_0\, \phi_1 \rangle$	$E_2(\phi_1)$	$\langle \phi_0\, \phi_1 \rangle$	$E_2(\phi_1)$	$\langle \phi_0 \phi_1 \rangle$	$E_2(\phi_1)$
3	0.2-6.0	-0.00015	-0.06540	-0.06982	-0.08627	-0.00385	-0.07157
3	0.2-8.0	-0.00270	-0.06475	--------	--------	--------	--------
3	0.2-10.0	-0.02309	-0.06372	--------	--------	--------	--------
4	0.2-6.0	-0.00063	-0.06503	-0.07261	-0.08668	-0.00095	-0.07156
4	0.2-8.0	+0.00002	-0.06495	--------	--------	--------	--------
4	0.2-10.0	+0.00671	-0.06524	--------	--------	--------	--------
5	0.2-6.0	-0.00203	-0.06479	-0.07807	-0.08782	+0.00003	-0.07180
5	0.2-8.0	-0.00260	-0.06280	--------	--------	--------	--------
5	0.2-10.0	-0.02018	-0.05267	--------	--------	--------	--------

Table A-III. Best χ_1 and ϕ_1 Extracted from the R-W Closed- and Open-Shell Functions[a].

Expansion Coefficients

Function		m = 0	m = 1	m = 2	m = 3	m = 4
γ_{1m},	closed-shell, Eq. (A-5)	-6.85438(-1)	4.57998(-1)	-6.67453(-2)	5.15773(-3)	-2.33259(-4)
α_{1m},	closed-shell, Eq. (A-10)	-1.68359(-1)	-1.48636(-2)	6.73491(-2)	-9.84627(-4)	-1.77761(-4)
γ_{1m},	open-shell, Eq. (A-5)	-6.48660(-1)	4.59509(-1)	-9.16084(-2)	-1.24098(-2)	-6.76246(-4)
α_{1m},	open-shell, Eq. (A-10)	-2.13050(-1)	-2.76269(-2)	1.38740(-1)	-1.95621(-2)	1.06825(-3)
β_{1m},	open-shell, Eq. (A-11)	-8.68962(-4)	-2.37916(-3)	1.81352(-1)	-4.32272(-2)	2.84416(-3)
λ_{1m},	closed-shell[b]	8.64865(-2)	4.32473(-2)	-4.67571(-3)	-8.63198(-5)	2.22201(-6)
λ_{1m},	(H-F)[c]	1.56250(-1)	7.81250(-2)	-5.20833(-3)	-3.25521(-4)	-1.62760(-5)

a. The number in parenthesis indicates the power of ten by which the corresponding entry is to be multiplied. For example, 6.73(-2) = 0.0673.

b. Expansion according to $\phi_1 = \pi^{-1} e^{(-\rho_1 - \rho_2)} \sum_{m=0}^{4} \lambda_{1m} \left[L_{m+1}(2\rho_1) + L_{m+1}(2\rho_2) \right]$

where $L_n(x) = -(n!)^2 \sum_{k=0}^{n-1} (-x)^k / (n-k-1)!(k+1)!k!$ are the Laguerre polynomials.

c. Laguerre expansion of ϕ_1(H-F) from reference 3. Allowance has been made for the different normalization used there.