the correlation function χ_N then achieves that the total wave function Φ_N given by Eq. (1) or (2) is normalized in the usual sense:

$$\int dV\Phi_N^2=1.$$

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Correlated Orbitals for the Ground State of the Hydrogen Molecule*

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INTRODUCTION

For the ground state of the helium atom and its isoelectronic series, wave functions constructed from a conventional orbital product, times a correlation function depending on the interelectronic distance only, have been relatively successful.[1] The best correlated closed shell, using the same orbital for both electrons, yields energies within 0.15 ev of experiment; the best correlated open shell, using a symmetrized product of two different orbitals, comes within 0.015 ev.

In this paper we give the results of similar calculations on the hydrogen molecule. The correlated closed shell for H_2 is represented by

$$\Phi_C=\varphi(1)\varphi(2)\chi(r_{12}), \tag{1}$$

where φ is a one-electron function or orbital, and $\chi(r_{12})$ is the correlation function. The orbital φ must be of species σ_g; expressing φ in terms of the usual elliptic coordinates,[2] this means that

$$\varphi(\xi,\eta)=\varphi(\xi,-\eta). \tag{2}$$

For the correlated open shell there are two different possibilities. They both have in common that the total wave function is given by

$$\Phi={}_0[\varphi(1)\psi(2)+\psi(1)\varphi(2)]\chi(r_{12}). \tag{3}$$

The difference between the two open shells is in the orbitals. One type, which we call the *in-out correlated open shell*, is built from a φ and ψ which both have σ_g symmetry and satisfy Eq. (2). For the other type, called the *left-right correlated open shell*, the orbitals φ and ψ have only cylindrical, or σ, symmetry, and they are each other's mirror image with respect to the center of the molecule.

The first correlated closed-shell calculation was done by Frost and Braunstein.[3] They used a simple LCAO for the orbital $\varphi=1s_a+1s_b$, and a two-term correlation function $\chi(r_{12})=1+cr_{12}$; the effective nuclear charge of the 1s orbitals and the constant c were the adjustable parameters. Their calculation yielded a binding energy which was still in error by 0.6 ev. Since we expect (from analogy with the helium series) only about 0.15 ev or less for well-adjusted orbital(s) and correlation function, Frost and Braunstein's choice for these was clearly too inflexible. We adopted the expressions

$$\begin{aligned}\varphi(\xi,\eta)&=\sum_{i=0}^{m}a_iu_i(\xi,\eta),\\ \psi(\xi,\eta)&=\sum_{i=0}^{m}b_iu_i(\xi,\eta),\\ \chi(r_{12})&=\sum_{\mu=0}^{n}c_\mu v_\mu(r_{12});\end{aligned} \tag{4}$$

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[1] C. C. J. Roothaan and A. W. Weiss, Revs. Modern Phys. 32, 194 (1960), this issue.

[2] If a and b refer to the two nuclei, and R is the internuclear distance, $\xi=(r_a+r_b)/R$, $\eta=(r_a-r_b)/R$.

[3] A. A. Frost and J. Braunstein, J. Chem. Phys. 19, 1133 (1951).

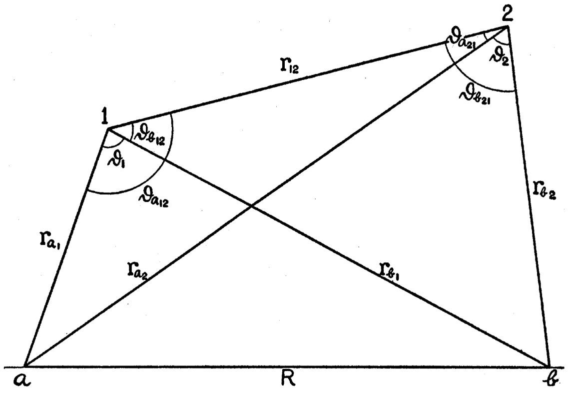

FIG. 1. Coordinate system.

the basis functions u_i and v_μ are given by

$$u_i(\xi,\eta)=\xi^{p_i}\eta^{q_i}e^{-\alpha\xi},\quad v_\mu(r_{12})=r_{12}{}^{\mu},\tag{5}$$

where p_i, q_i are two integers, which are functions of i, and q_i is *even*. Hence we deal only with the correlated closed shell and the in-out correlated open shell. The reason for this restriction was that these two cases are formally identical with the helium series calculations[1] once the supermatrix elements have been constructed; hence the only new computer programs needed were those for calculating the primitive integrals and subsequently the supermatrix elements. The left-right correlated open shell is also an interesting wave function form and should perhaps be investigated at some future date.

SINGULARITIES IN THE WAVE FUNCTION AND THE HAMILTONIAN

For a four-particle system, the ground-state wave function depends on the six interparticle distances only, which may be taken as the independent coordinates. The total Hamiltonian is, in general,[4]

$$\mathcal{H}=\sum_{i<j}\left[-\frac{1}{2}\left(\frac{1}{m_i}+\frac{1}{m_j}\right)\left(\frac{\partial^2}{\partial r_{ij}{}^2}+\frac{2}{r_{ij}}\frac{\partial}{\partial r_{ij}}\right)+\frac{Z_iZ_j}{r_{ij}}\right]-\sum_{i\neq j,k;\,j<k}\frac{1}{m_i}\cos(\mathbf{r}_{ij},\mathbf{r}_{ik})\frac{\partial^2}{\partial r_{ij}\partial r_{ik}},\tag{6}$$

where m_i and Z_i are the mass and charge of the ith particle.

The Hamiltonian (6) suggests that the wave function be put forward as a product of the interparticle distances. However, in a molecular case it is more customary to start with the Born-Oppenheimer approximation, which is obtained by giving the nuclei infinite masses and fixed positions, and considering the electronic wave function for the fixed nuclear framework. We transform the Hamiltonian (6) accordingly. We change the subscripts 3 and 4 into a and b, referring to the nuclei in more conventional notation. We further put $m_1=m_2=1$, $m_a=m_b=\infty$, $-Z_1=-Z_2=Z_a=Z_b=1$, $r_{ab}=R$, and introduce the elliptic coordinates ξ and η; the Hamiltonian then becomes

$$\mathcal{H}=\mathcal{H}_1+\mathcal{H}_2+\mathcal{H}_{12}+\mathcal{H}_{12}{}',\tag{7}$$

where (see Fig. 1)

$$\mathcal{H}_i=-\frac{2}{R^2(\xi_i{}^2-\eta_i{}^2)}\left[(\xi_i{}^2-1)\frac{\partial^2}{\partial\xi_i{}^2}+(1-\eta_i{}^2)\frac{\partial^2}{\partial\eta_i{}^2}+2\xi_i\frac{\partial}{\partial\xi_i}-2\eta_i\frac{\partial}{\partial\eta_i}+2R\xi_i\right],$$

$$\mathcal{H}_{12}=-\left(\frac{\partial^2}{\partial r_{12}{}^2}+\frac{2}{r_{12}}\frac{\partial}{\partial r_{12}}-\frac{1}{r_{12}}\right),$$

$$\begin{aligned}\mathcal{H}_{12}{}'=-\frac{1}{R}\Big[&(\cos\vartheta_{a12}+\cos\vartheta_{b12})\frac{\partial}{\partial\xi_1}\\&+(\cos\vartheta_{a12}-\cos\vartheta_{b12})\frac{\partial}{\partial\eta_1}\\&+(\cos\vartheta_{a21}+\cos\vartheta_{b21})\frac{\partial}{\partial\xi_2}\\&+(\cos\vartheta_{a21}-\cos\vartheta_{b21})\frac{\partial}{\partial\eta_2}\Big]\frac{\partial}{\partial r_{12}}.\end{aligned}\tag{8}$$

We note that $(\xi_i^2-1)/(\xi_i^2-\eta_i^2)=\frac{1}{2}(1+\cos\theta_i)$, $(1-\eta_i^2)/(\xi_i^2-\eta_i^2)=\frac{1}{2}(1-\cos\theta_i)$ (see Fig. 1). If Φ is an approximate wave function, the expression $\mathcal{H}\Phi/\Phi$ has, in general, *infinite* singularities for $r_{12}=0$ due to the last two terms of $\mathcal{H}_{12}$, and for $\xi_i=1$, $\eta_i=\pm1$ (which corresponds to $r_{bi}=0$ and $r_{a1}=0$, respectively) due to the last three terms of $\mathcal{H}_i$; furthermore, *bounded* singularities can occur due to the first two terms of $\mathcal{H}_i$, and all the terms of $\mathcal{H}_{12}{}'$. The conditions that the infinite singularities cancel are

$$\begin{aligned}\left[\frac{1}{\Phi}\left(\xi_i\frac{\partial\Phi}{\partial\xi_i}-\eta_i\frac{\partial\Phi}{\partial\eta_i}\right)+R\xi_i\right]_{\xi_i=1,\,\eta_i=\pm1}&=0,\\ \left[\frac{1}{\Phi}\frac{\partial\Phi}{\partial r_{12}}-\frac{1}{2}\right]_{r_{12}=0}&=0.\end{aligned}\tag{9}$$

The correlated closed- and open-shell wave functions (1) and (3) satisfy the conditions (9) if the orbital(s) and correlation function satisfy the *cusp conditions*

$$\frac{1}{R}\left[\frac{1}{\varphi}\left(\frac{\partial\varphi}{\partial\xi}-\frac{\partial\varphi}{\partial\eta}\right)\right]_{\xi=1,\eta=1}=\frac{1}{R}\left[\frac{1}{\psi}\left(\frac{\partial\psi}{\partial\xi}-\frac{\partial\psi}{\partial\eta}\right)\right]_{\xi=1,\eta=1}=1,\tag{10}$$

$$[(1/\chi)(\partial\chi/\partial r)]_{r=0}=\tfrac{1}{2};$$

---

[4] This form of the Hamiltonian was recently introduced by A. A. Frost (private communication).

for our explicit expansions (4), (5), this becomes

$$\frac{1}{R}\Big[\alpha-\sum_i(p_i-q_i)a_i\Big/\sum_i a_i\Big]$$

$$=\frac{1}{R}\Big[\alpha-\sum_i(p_i-q_i)b_i\Big/\sum_i b_i\Big]=1, \quad (11)$$

$$(c_1/c_0)=\tfrac{1}{2}.$$

ITERATIVE EQUATIONS FOR EXPANSION COEFFICIENTS AND EVALUATION OF SUPERMATRIX ELEMENTS

The formalism for determining the best coefficients for the orbital(s) and correlation function is almost identical with that developed for the helium series. In particular, we can take over Eqs. (12)–(21) from footnote reference 1 if we replace the potential energy operator $-Z(1/r_1+1/r_2)+1/r_{12}$ by $-1/r_{a1}-1/r_{b1}-1/r_{a2}-1/r_{b2}+1/r_{12}$. The derivation of the supermatrix elements in terms of primitive integrals is a somewhat lengthy but straightforward and well-known process: the results are

$$\begin{aligned}H_{ijkl\mu\nu}=2R^{-2}\big[&\alpha^2(K_{p+2,q\bar{p}\bar{q}}{}^{\mu+\nu}+K_{\bar{p}+2,\bar{q}pq}{}^{\mu+\nu}\\&-K_{pq\bar{p}\bar{q}}{}^{\mu+\nu}-K_{\bar{p}\bar{q}pq}{}^{\mu+\nu})-\alpha p(K_{p+1,q\bar{p}\bar{q}}{}^{\mu+\nu}\\&-K_{p-1,q\bar{p}\bar{q}}{}^{\mu+\nu})-\alpha\bar{p}(K_{\bar{p}+1,\bar{q}pq}{}^{\mu+\nu}-K_{\bar{p}-1,\bar{q}pq}{}^{\mu+\nu})\\&+(p_ip_j-q_iq_j)K_{pq\bar{p}\bar{q}}{}^{\mu+\nu}+(p_kp_l-q_kq_l)K_{\bar{p}\bar{q}pq}{}^{\mu+\nu}\\&-p_ip_jK_{p-2,q\bar{p}\bar{q}}{}^{\mu+\nu}-p_kp_lK_{\bar{p}-2,\bar{q}pq}{}^{\mu+\nu}\\&+q_iq_jK_{p,q-2,\bar{p}\bar{q}}{}^{\mu+\nu}+q_kq_lK_{\bar{p},\bar{q}-2,pq}{}^{\mu+\nu}\big]\\&-\tfrac{1}{2}[\mu(\mu+1)+\nu(\nu+1)](K_{p+2,q\bar{p}\bar{q}}{}^{\mu+\nu-2}\\&-K_{p,q+2,\bar{p}\bar{q}}{}^{\mu+\nu-2})\\&-4R^{-1}(K_{p+1,q\bar{p}\bar{q}}{}^{\mu+\nu}+K_{\bar{p}+1,\bar{q}pq}{}^{\mu+\nu})\\&\qquad+(K_{p+2,q\bar{p}\bar{q}}{}^{\mu+\nu-1}-K_{p,q+2,\bar{p}\bar{q}}{}^{\mu+\nu-1}),\end{aligned}\quad (12)$$

$$S_{ijkl\mu\nu}=K_{p+2,q\bar{p}\bar{q}}{}^{\mu+\nu}-K_{p,q+2,\bar{p}\bar{q}}{}^{\mu+\nu}, \quad (13)$$

where

$$p=p_i+p_j,\quad \bar{p}=p_k+p_l,\quad q=q_i+q_j,\quad \bar{q}=q_k+q_l,$$

and the primitive integrals $K_{pq\bar{p}\bar{q}}{}^{\mu}$ are given by

$$K_{pq\bar{p}\bar{q}}{}^{\mu}=\int\int dV_1dV_2(\xi_1{}^2-\eta_1{}^2)^{-1}\times e^{-2\alpha(\xi_1+\xi_2)}\xi_1{}^p\eta_1{}^q\xi_2{}^{\bar{p}}\eta_2{}^{\bar{q}}r_{12}{}^{\mu}; \quad (14)$$

note that

$$K_{p+2,q\bar{p}\bar{q}}{}^{\mu}-K_{p,q+2,\bar{p}\bar{q}}{}^{\mu}=K_{\bar{p}+2,\bar{q}pq}{}^{\mu}-K_{\bar{p},\bar{q}+2,pq}{}^{\mu}. \quad (15)$$

EVALUATION OF THE PRIMITIVE INTEGRALS

The integrals $K_{pq\bar{p}\bar{q}}{}^{\mu}$ are evaluated using the methods developed by James and Coolidge,[5] Kotani et al.,[6] and Ruedenberg.[7] For even μ they are expressible as linear combinations of products of one-electron integrals; for odd μ they can all be reduced to $K_{pq\bar{p}\bar{q}}{}^{-1}$, and they require the Neumann expansion for $r_{12}{}^{-1}$ in elliptic coordinates. In our calculations the highest power of r_{12} in the correlation function was taken to be 2. This seems somewhat low in view of the results for the helium series[1]; taking higher powers, however, would have materially increased the complexity of the calculations. Hence we have to evaluate $K_{pq\bar{p}\bar{q}}{}^{\mu}$ for $\mu=-1$, 0, 1, 2, 3, 4. Since we deal only with the correlated closed shell and the in-out correlated open shell, it is easily seen that only integrals $K_{pq\bar{p}\bar{q}}{}^{\mu}$ with even q and $\bar{q}$ are needed. However, the integrals with odd q and $\bar{q}$ are useful in calculations with slightly different types of wave function, and we shall give the formulas for the general case.

We later make use of the relation

$$\begin{aligned}r_{12}{}^2=\tfrac{1}{4}R^2\{&\xi_1{}^2+\eta_1{}^2+\xi_2{}^2+\eta_2{}^2-2\xi_1\eta_1\xi_2\eta_2-2\\&-2[(\xi_1{}^2-1)(1-\eta_1{}^2)(\xi_2{}^2-1)(1-\eta_2{}^2)]^{\frac{1}{2}}\\&\times\cos(\varphi_1-\varphi_2)\}.\end{aligned}\quad (16)$$

We define the charge distributions

$$\Sigma_{1pq}=e^{-2\alpha\xi}\xi^p\eta^q, \quad (17)$$

and

$$\left.\begin{aligned}\Sigma_2&=(\xi^2+\eta^2-1)\Sigma_1,\\\Sigma_3&=(\xi^2+\eta^2-1)^2\Sigma_1,\\\Sigma_4&=\xi\eta\Sigma_1,\\\Sigma_5&=\xi^2\eta^2\Sigma_1,\\\Sigma_6&=\xi\eta(\xi^2+\eta^2-1)\Sigma_1,\\\Sigma_7&=(\xi^2-1)(1-\eta^2)\Sigma_1,\\\Pi_1&=[(\xi^2-1)(1-\eta^2)]^{\frac{1}{2}}\cos\varphi\Sigma_1,\\\Pi_2&=(\xi^2+\eta^2-1)\Pi_1,\\\Pi_3&=\xi\eta\Pi_1,\\\Delta_1&=(\xi^2-1)(1-\eta^2)\cos2\varphi\Sigma_1;\end{aligned}\right\}\quad (18)$$

in Eqs. (18) we suppressed the indices p and q, hence $\Sigma_{4pq}=\xi\eta\Sigma_{1pq}$, etc. Similarly, we define a set of additional charge distributions by

$$\Sigma_1{}^*=(\xi^2-\eta^2)\Sigma_1, \quad (19)$$

and similarly, $\Sigma_2{}^*$, $\Sigma_3{}^*$, etc.

By using Eqs. (14), (16) and the definitions (17)–(19), we can now express the primitive integrals in terms of integrals over the charge distributions. After

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

[6] M. Kotani, A. Amemiya, E. Ishiguro, and T. Kimura, *Tables of Molecular Integrals* (Maruzen Company, Tokyo, 1955).

[7] K. Ruedenberg, J. Chem. Phys. **19**, 1459 (1951).

TABLE I. Closed shell, no correlation function (SCF).

α	0.75	0.85	0.90	0.95	1.00
E_{el}(a.u.)	−1.84745	−1.84775	−1.84782	−1.84786	−1.84785
E_{tot}(a.u.)	−1.13317	−1.13347	−1.13354	−1.13357	−1.13356
D(ev)	3.6235	3.6316	3.6335	3.6344	3.6341
ξ η					
0 0	1.00000	1.00000	1.00000	1.00000	1.00000
1 0	−0.13123	−0.06305	−0.03191	−0.00626	0.01106
2 0	0.01283	0.01561	0.02083	0.02980	0.04338
0 2	0.27427	0.28636	0.28869	0.28781	0.28322
1 2	−0.03790	−0.02685	−0.01816	−0.00724	0.00588
Cusp	−0.929	−0.948	−0.955	−0.961	−0.966

some manipulations, this becomes, symbolically,

$$
\begin{aligned}
K^0&=\langle\Sigma_1|\Sigma_1{}^*\rangle,\\
4R^{-2}K^2&=\langle\Sigma_2|\Sigma_1{}^*\rangle+\langle\Sigma_1|\Sigma_2{}^*\rangle-2\langle\Sigma_4|\Sigma_4{}^*\rangle,\\
16R^{-4}K^4&=\langle\Sigma_3|\Sigma_1{}^*\rangle+\langle\Sigma_1|\Sigma_3{}^*\rangle+2\langle\Sigma_2|\Sigma_2{}^*\rangle\\
&\quad-4\langle\Sigma_6|\Sigma_4{}^*\rangle-4\langle\Sigma_4|\Sigma_6{}^*\rangle\\
&\quad+4\langle\Sigma_5|\Sigma_5{}^*\rangle+2\langle\Sigma_7|\Sigma_7{}^*\rangle, \qquad (20)\\
K^{-1}&=[\Sigma_1|\Sigma_1{}^*],\\
4R^{-2}K^1&=[\Sigma_2|\Sigma_1{}^*]+[\Sigma_1|\Sigma_2{}^*]\\
&\quad-2[\Sigma_4|\Sigma_4{}^*]-4[\Pi_1|\Pi_1{}^*],\\
16R^{-4}K^3&=[\Sigma_3|\Sigma_1{}^*]+[\Sigma_1|\Sigma_3{}^*]+2[\Sigma_2|\Sigma_2{}^*]\\
&\quad-4[\Sigma_6|\Sigma_4{}^*]-4[\Sigma_4|\Sigma_6{}^*]+4[\Sigma_5|\Sigma_5{}^*]\\
&\quad+2[\Sigma_7|\Sigma_7{}^*]-8[\Pi_2|\Pi_1{}^*]-8[\Pi_1|\Pi_2{}^*]\\
&\quad+16[\Pi_3|\Pi_3{}^*]+4[\Delta_1|\Delta_1{}^*].
\end{aligned}
$$

In Eqs. (20) we have suppressed the indices p, q, $\bar{p}$, $\bar{q}$; the first Eq. (20) written out in full would read

$$K_{pq\bar{p}\bar{q}}{}^0=\langle\Sigma_{1pq}|\Sigma_{1\bar{p}\bar{q}}{}^*\rangle,$$

and the others are analogous. Finally, the symbols $\langle\Psi|\Omega^*\rangle$ and $[\Psi|\Omega^*]$ are defined by

$$
\begin{aligned}
\langle\Psi|\Omega^*\rangle&=\int\!\!\int dV_1dV_2(\xi_1{}^2-\eta_1{}^2)^{-1}(\xi_2{}^2-\eta_2{}^2)^{-1}\\
&\qquad\times\Psi(1)\Omega^*(2),\\
[\Psi|\Omega^*]&=\int\!\!\int dV_1dV_2(\xi_1{}^2-\eta_1{}^2)^{-1}(\xi_2{}^2-\eta_2{}^2)^{-1}\\
&\qquad\times\Psi(1)\Omega^*(2)r_{12}{}^{-1},
\end{aligned}
\qquad (21)
$$

where Ω,Ψ stand for any of the symbols Σ_1, $\Sigma_2,\cdots\Delta_1$.

We now turn to the final quadratures. We write for the charge distributions in general

$$
\begin{aligned}
\Sigma_{\kappa pq}&=e^{-2\alpha\xi}\sum_{rs}\sigma_{\kappa rs}\xi^{p+r}\eta^{q+s},\\
\Pi_{\kappa pq}&=e^{-2\alpha\xi}\sum_{rs}\pi_{\kappa rs}\xi^{p+r}\eta^{q+s}[(\xi^2-1)(1-\eta^2)]^{\frac{1}{2}}\cos\varphi, \qquad (22)\\
\Delta_{1pq}&=e^{-2\alpha\xi}\sum_{rs}\delta_{1rs}\xi^{p+r}\eta^{q+s}(\xi^2-1)(1-\eta^2)\cos 2\varphi,
\end{aligned}
$$

where $\sigma_{\kappa rs}$, $\pi_{\kappa rs}$, δ_{1rs} are the coefficients of the small polynomials in Eqs. (18).

The integrals $\langle\Sigma_\kappa|\Sigma_\lambda{}^*\rangle$ which occur for K^μ with even μ can be evaluated in elementary fashion since the integrand factors completely. The result is

$$\langle\Sigma_{\kappa pq}|\Sigma_{\lambda\bar{p}\bar{q}}{}^*\rangle=\tfrac{1}{4}\pi^2R^6Q_{\kappa pq}Q_{\lambda\bar{p}\bar{q}}{}^*, \qquad (23)$$

where in general

$$Q_{\kappa pq}=\tfrac{1}{2}\sum_{rs}\sigma_{\kappa rs}\int_1^\infty d\xi e^{-2\alpha\xi}\xi^{p+r}\int_{-1}^1 d\eta\eta^{q+s}. \qquad (24)$$

The second integral in Eq. (24) vanishes for $q+s$ odd, and is equal to $2(q+s+1)^{-1}$ for $q+s$ even. Inspection of Eqs. (18) shows that Σ_4 and Σ_6 are even in $q+s$ if q is odd, and Σ_1, Σ_2, Σ_3, Σ_5, Σ_7 are even if q is even. Hence we obtain

$$Q_{\kappa pq}=\sum_{rs}\sigma_{\kappa rs}(q+s+1)^{-1}A_{p+r}(2\alpha) \qquad (25)$$

for $\kappa=4$, 6 and q odd, and for $\kappa=1$, 2, 3, 5, 7, and q even; otherwise $Q_{\kappa pq}$ vanishes. The function $A_n(x)$ is given by

$$A_n(x)=\int_1^\infty dte^{-xt}t^n=n!x^{-n-1}e^{-x}\sum_{k=0}^n x^k/k!. \qquad (26)$$

The integrals $[\Sigma_\kappa|\Sigma_\lambda{}^*]$, etc., which occur for K^μ with odd μ are more complicated. We follow closely Ruedenberg's treatment of the exchange integrals.[7] We substitute the Neumann expansion for $r_{12}{}^{-1}$ into the integrands and carry out the integrations over η_1, η_2, φ_1, φ_2; the results are

$$
\begin{aligned}
[\Sigma_{\kappa pq}|\Sigma_{\lambda\bar{p}\bar{q}}{}^*]&=\tfrac{1}{4}\pi^2R^5\sum_L\sum_{r\bar{r}}\sum_{s\bar{s}}\sigma_{\kappa rs}\sigma_{\lambda\bar{r}\bar{s}}{}^*\\
&\qquad\times B_{q+s}{}^{0L}B_{\bar{q}+\bar{s}}{}^{0L}\Phi_{p+r,\,\bar{p}+\bar{r}}{}^{0L}(2\alpha),\\
[\Pi_{\kappa pq}|\Pi_{\lambda\bar{p}\bar{q}}{}^*]&=\tfrac{1}{8}\pi^2R^5\sum_L\sum_{r\bar{r}}\sum_{s\bar{s}}\pi_{\kappa rs}\pi_{\lambda\bar{r}\bar{s}}{}^*\\
&\qquad\times B_{q+s}{}^{1L}B_{\bar{q}+\bar{s}}{}^{1L}\Phi_{p+r,\,\bar{p}+\bar{r}}{}^{1L}(2\alpha),\\
[\Delta_{1pq}|\Delta_{1\bar{p}\bar{q}}{}^*]&=\tfrac{1}{8}\pi^2R^5\sum_L\sum_{r\bar{r}}\sum_{s\bar{s}}\delta_{1rs}\delta_{1\bar{r}\bar{s}}{}^*\\
&\qquad\times B_{q+s}{}^{2L}B_{\bar{q}+\bar{s}}{}^{2L}\Phi_{p+r,\,\bar{p}+\bar{r}}{}^{2L}(2\alpha),
\end{aligned}
\qquad (27)
$$

TABLE II. Open shell, no correlation function.

α	0.75	0.85	0.90	0.95	1.00
E_{el}(a.u.)	−1.85542	−1.85597	−1.85607	−1.85611	−1.85608
E_{tot}(a.u.)	−1.14114	−1.14168	−1.14178	−1.14182	−1.14179
D(ev)	3.8403	3.8551	3.8579	3.8589	3.8582
ξ η					
0 0	1.00000	1.00000	1.00000	1.00000	1.00000
1 0	−0.31768	−0.28665	−0.26420	−0.23710	−0.20560
2 0	0.02997	0.02832	0.02675	0.02484	0.02280
0 2	0.15183	0.15569	0.15768	0.15928	0.16038
1 2	−0.02816	−0.02559	−0.02325	−0.01996	−0.01559
Cusp	−0.991	−1.030	−1.043	−1.053	−1.060
0 0	1.00000	1.00000	1.00000	1.00000	1.00000
1 0	0.09346	1.73166	1.98733	1.95636	1.62369
2 0	−0.00773	−0.06323	0.00585	0.12519	0.26870
0 2	0.09657	1.33218	1.43283	1.39648	1.22629
1 2	−0.00835	−0.01612	0.05432	0.13715	0.20952
Cusp	−0.814	−0.794	−0.775	−0.791	−0.796

TABLE III. Closed shell, two-term correlation function.

α	0.75	0.85	0.90	0.95	1.00
E_{el}(a.u.)	−1.88549	−1.88630	−1.88639	−1.88642	−1.88642
E_{tot}(a.u.)	−1.17120	−1.17201	−1.17211	−1.17214	−1.17214
D(ev)	4.6584	4.6805	4.6830	4.6838	4.6838
ξ η					
0 0	1.00000	1.00000	1.00000	1.00000	1.00000
1 0	−0.20991	−0.15172	−0.11642	−0.07919	−0.04227
2 0	0.01584	0.01263	0.01161	0.01186	0.01420
0 2	0.21493	0.22466	0.22828	0.23038	0.23041
1 2	−0.03131	−0.02514	−0.01965	−0.01226	−0.00279
Cusp	−0.963	−0.978	−0.992	−0.992	−0.995
r_{12}					
0	1.00000	1.00000	1.00000	1.00000	1.00000
1	0.41751	0.43270	0.43463	0.43518	0.43536

where

$$B_q^{ML}=\begin{cases}\left[\dfrac{2}{(2L+1)}\dfrac{(L+M)!}{(L-M)!}\right]^{\frac{1}{2}}\dfrac{2^Lq!}{(q+L+M+1)!}\\ \quad\times\dfrac{[\frac{1}{2}(q+L+M)]!}{[\frac{1}{2}(q-L+M)]!}, \\ \quad\text{for } q-L+M\geqslant 0 \text{ and even,} \\ 0 \quad \text{otherwise;}\end{cases} \tag{28}$$

$$\Phi_{p\bar{p}}^{ML}(x)=\int_1^\infty d\xi(\xi^2-1)^{-1}f_p^{ML}(\xi,x)f_{\bar{p}}^{ML}(\xi,x), \tag{29}$$

$$f_p^{ML}(\xi,x)=[P_L^M(\xi)]^{-1}\int_1^\xi dtP_L^M(t)(t^2-1)^{\frac{1}{2}M} \times e^{-xt}t^p. \tag{30}$$

Note that the condition that B_0^{ML} be finite, expressed in Eq. (28), guarantees that the sums over L in Eqs. (27) remain finite. For details of the derivation of Eqs. (27)–(30) the reader is referred to Ruedenberg's paper.[7]

For $M=0$ the $\Phi_{p\bar{p}}^{ML}$ were evaluated by numerical integration using Eqs. (29) and (30). A 50-point integration gave 6–7 significant figures. Checks were made against values tabulated by Kotani et al.[6] For $M\geqslant 1$ the recurrence relation

$$\Phi_{p\bar{p}}^{M+1,L}=\Phi_{p+1,\bar{p}+1}^{ML}-\frac{(L+M)}{(2L+1)}\Phi_{p\bar{p}}^{M,L-1}-\frac{(L-M+1)}{(2L+1)}\Phi_{p\bar{p}}^{M,L+1} \tag{31}$$

was used.

TABLE IV. Open shell, two-term correlation function.

α	0.75	0.85	0.90	0.95	1.00
E_{el}(a.u.)	−1.88614	−1.88687	−1.88694	−1.88696	−1.88696
E_{tot}(a.u.)	−1.17186	−1.17258	−1.17266	−1.17268	−1.17268
D(ev)	4.6762	4.6959	4.6980	4.6986	4.6986
ξ η					
0 0	1.00000	1.00000	1.00000	1.00000	1.00000
1 0	−0.28817	−0.24364	−0.20992	−0.16727	−0.11649
2 0	0.02371	0.01913	0.01538	0.01036	0.00464
0 2	0.18445	0.19481	0.19903	0.20022	0.20368
1 2	−0.03152	−0.02886	−0.02554	−0.01979	−0.01316
Cusp	−1.001	−1.036	−1.045	−1.045	−1.038
0 0	1.00000	1.00000	1.00000	1.00000	1.00000
1 0	−0.05691	0.03913	0.08186	0.10685	0.11217
2 0	0.00055	0.00109	0.00318	0.01392	0.03154
0 2	0.27888	0.29235	0.29584	0.29873	0.29006
1 2	−0.03216	−0.01908	−0.00909	0.00164	0.01621
Cusp	−0.885	−0.895	−0.900	−0.911	−0.922
r_{12}					
0	1.00000	1.00000	1.00000	1.00000	1.00000
1	0.39050	0.40319	0.40488	0.40574	0.40618

TABLE V. Closed Shell, three-term correlation function.

α	0.75	0.85	0.90	0.95	1.00
E_{el}(a.u.)	−1.88597	−1.88673	−1.88682	−1.88685	−1.88684
E_{tot}(a.u.)	−1.17168	−1.17244	−1.17254	−1.17257	−1.17255
D(ev)	4.6715	4.6921	4.6947	4.6955	4.6952
ξ η					
0 0	1.00000	1.00000	1.00000	1.00000	1.00000
1 0	−0.21072	−0.15402	−0.12103	−0.08703	−0.05395
2 0	0.01726	0.01490	0.01473	0.01604	0.01957
0 2	0.21762	0.22567	0.22821	0.22907	0.22785
1 2	−0.03088	−0.02359	−0.01751	−0.00955	0.00039
Cusp	−0.953	−0.978	−0.986	−0.992	−0.996
r_{12}					
0	1.00000	1.00000	1.00000	1.00000	1.00000
1	0.52184	0.52885	0.53026	0.52980	0.52782
2	−0.03203	−0.03025	−0.03012	−0.02972	−0.02903

RESULTS AND DISCUSSION

The computations were carried out on the Remington Rand Univac Scientific 1103 computer at Wright-Patterson Air Force Base. As mentioned before, the expansion length for the correlation function was restricted to three terms ($n=0, 1, 2$). The orbitals were restricted to 5 terms ($m=2$). The latter restriction was necessary due to the size of the memory. Since Coulson[8] obtained good results for the SCF function of H_2 with these 5 terms, this restriction should not be serious for the closed-shell calculations. For the open-shell calculations these 5 terms probably are not sufficient to allow the two orbitals to be optimized; indeed, the improvement of the open shell over the closed shell is in this case not as large as for the helium series.[1] The

TABLE VI. Open shell, three-term correlation function.

α	0.75	0.85	0.90	0.95	1.00
E_{el}(a.u.)	−1.88644	−1.88713	−1.88722	−1.88724	−1.88724
E_{tot}(a.u.)	−1.17215	−1.17285	−1.17293	−1.17296	−1.17295
D(ev)	4.6843	4.7032	4.7054	4.7061	4.7059
ξ η					
0 0	1.00000	1.00000	1.00000	1.00000	1.00000
1 0	−0.27951	−0.22158	−0.17779	−0.12579	−0.06314
2 0	0.02293	0.01600	0.01033	0.00387	−0.00376
0 2	0.20474	0.21418	0.21952	0.22720	0.22989
1 2	−0.03571	−0.03150	−0.02697	−0.02234	−0.01363
Cusp	−1.011	−1.036	−1.039	−1.041	−1.024
0 0	1.00000	1.00000	1.00000	1.00000	1.00000
1 0	−0.08591	−0.02855	−0.01546	−0.01229	−0.02490
2 0	0.00616	0.01101	0.01970	0.03264	0.05120
0 2	0.24432	0.25141	0.24912	0.23921	0.23212
1 2	−0.02391	−0.01179	−0.00354	0.00889	0.01960
Cusp	−0.873	−0.898	−0.912	−0.923	−0.941
r_{12}					
0	1.00000	1.00000	1.00000	1.00000	1.00000
1	0.47632	0.48526	0.48883	0.49012	0.48972
2	−0.02486	−0.02376	−0.02412	−0.02416	−0.02381

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[8] C. A. Coulson, Proc. Cambridge Phil. Soc. 34, 204 (1938).

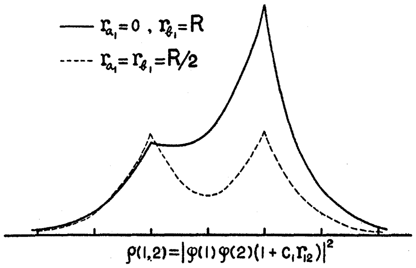

FIG. 2. Probability density of the second electron along the axis for two fixed locations of the first electron.

calculations were carried out for $R=1.4$ a.u.; according to the most recent values[9] for the fundamental constants this is 0.74084 A, which is close enough for our purpose to the experimental[10] equilibrium distance

$$R_e=0.74116 \text{ A}.$$

TABLE VII. Energies and cusp values for $\alpha=0.95$.

m	Form	E_{el}(a.u.)	E_{tot}(a.u.)	D(ev)	Orb. cusp	Corr. cusp
0	Closed	−1.84786	−1.13357	3.6344	−0.961	...
	Open	−1.85611	−1.14182	3.8589	−1.053, −0.791	...
1	Closed	−1.88642	−1.17214	4.6838	−0.992	0.435
	Open	−1.88696	−1.17268	4.6986	−1.045, −0.911	0.406
2	Closed	−1.88685	−1.17257	4.6955	−0.992	0.530
	Open	−1.88724	−1.17296	4.7061	−1.041, −0.923	0.490
	Exptl.			4.7466		

The exponent α and the expansion length of the correlation function were varied; the results of the computations are summarized in Tables I–VI. It appears that the optimum α is between 0.95 and 1.00 for all cases, and E versus α is very shallow around the minimum; for ease of comparison, the energies and cusp values for $\alpha=0.95$ are collected in Table VII. The closed-shell calculation with a single term for the correlation function is identical with the SCF calculation; our value is slightly lower than Coulson's due to the optimization of α. The cusp values obtained indicate that the expansion lengths are not as satisfactory as in the helium-series calculations.[1] In spite of this, however, the best energies obtained are rather good: 4.6955 ev for the closed shell, 4.7061 ev for the open shell, compared to the experimental value[11] 4.7466±0.0007 ev. It is to be noted that the best closed-shell energy for H_2 is *closer* to the experimental value than for helium; on the other hand, our best open-shell energy is inferior to that for helium, which is probably due to the short expansions for the orbitals. Figure 2 illustrates how the correlated orbital wave function helps the electrons to avoid each other. For the case of the closed-shell function and $n=1$, we plotted the probability density of electron 2 along the molecular axis for two fixed locations of electron 1: at the midpoint (dotted curve) and on atom a (full curve). The latter curve shows that if one electron is on atom a, the other electron is most likely to be found on atom b, as it should be.

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[11] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950).