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Evaluation of Two-Center, Two-Electron Integrals

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Abstract: We present a new analytic treatment of two-electron integrals over two-center integrals including correlation (interelectronic distance) explicitly in the wave function. All the integrals needed for the evaluation of the matrix elements of any diatomic two-electron molecule are obtained as analytic recursion expressions. As an application of this method in molecular physics, we calculate the value of the ground-state energy and equilibrium internuclear distance of the hydrogen molecule in the Born−Oppenheimer approximation.

1. Introduction

Two-center, two-electron systems are a subject of great interest in molecular physics. In particular, several molecules may be described as such a system. Computation of the Born−Oppenheimer ground-state energy of the hydrogen molecule was the subject of progressively more accurate variational calculations.[1−5] Two-electron addition to closed-shell neutral polar molecules may also be described as a two-center, two-electron system. The binding of two electrons to a fixed finite dipole has not been resolved. In recent years, there has been increasing interest in the study of the possible existence of such dipole-bound dianions.[6−9] The study of this kind of weakly bound states represents an interesting field of research. For these states, the energy is nonanalytical as a function of the dipolar moment, and a bound state could not exist at the threshold energy; therefore, they might be good candidates to be halo states.[10] Technical problems appear when standard approximations such as perturbation theory, nonlinear variational calculations, or the Rayleigh−Ritz method are used to study weakly bound states.[11] Recently, a finite size-scaling theory for the study of near-threshold properties in quantum few-body problems has been developed.[12] The method was successfully applied to one electron attached to dipole and quadrupole potentials.[13,14] An accurate expansion of the ground-state wave function in a (truncated) complete basis-set is necessary in order to apply finite size-scaling methods to two-center, two-electron systems.

James and Coolidge[1] were the first that made ab initio calculations for two-center, two-electron systems using correlated functions. These functions include the interelectronic coordinate explicitly. They extend the method used by Hylleraas for the helium atom[15] to the hydrogen molecule. After this, many authors used the James−Coolidge or modified James−Coolidge expansions for the calculation of different properties of diatomic two-electron systems.[2,4,5]

Even if the results obtained using James−Coolidge expansion are very accurate, this method has some difficulties. The inclusion of the interelectronic coordinate (as powers) in the wave function generates very complicated two-electron, two-center integrals. Kolos et al.[2,4] solved these integrals keeping powers of the interelectronic distance up to order three and obtained very accurate values for the ground-state energy of the hydrogen molecule.[4] In ref 16, Kolos and Roothaan present an interesting treatment of these integrals. They solve fully analytically the case of even powers of the interelectronic distance. The case of odd powers was partially solved and completed with numerical integration.

The aim of this paper is to report a new method for the analytical evaluation of the two-electron, two-center James−Coolidge integrals without limitation in the power of the correlation coordinate.

This paper is organized as follows. In section 2, we develop our method for the evaluation of two-center, two-electron integrals and we express these integrals as analytical recurrence relations. Technical aspects are discussed and numerical evaluations are presented in section 3. In section 4, we apply the results obtained in previous sections to

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evaluate the ground-state energy of the hydrogen molecule. Finally, our conclusions are given in section 5.

2. Two-Electron Integrals over Two-Center Orbitals

The basic integrals that appear in a two-center, two-electron James−Coolidge ground-state expansion of any diatomic two-electron system are of the form[2]

$$I^m_{pqrs} = \left(\frac{2}{R}\right)^6 \int d^3x_1\, d^3x_2\, \frac{e^{-(\alpha\xi_1+\beta\xi_2)}}{\xi_1^2-\eta_1^2}\xi_1^p\eta_1^q\xi_2^r\eta_2^s r_{12}^m \qquad (1)$$

where the integral is expressed in usual prolate spheroidal coordinates (ξ, η, and ϕ)[17]. ϕ is the azimuthal angle, $\xi = (r_a + r_b)/R$, $\eta = (r_a - r_b)/R$, r_a and r_b are the distances to the centers, R represents the distance between centers, r_{12} is the interelectronic distance, and α and β are variational parameters. Powers are integer numbers with $p, q, r, s \geq 0$ and $m \geq -1$.

Introducing the auxiliary integral

$$g_{pqrs}(k) = \left(\frac{2}{R}\right)^6 \int d^3x_1\, d^3x_2\, \frac{e^{-(\alpha\xi_1+\beta\xi_2)}}{\xi_1^2-\eta_1^2}\xi_1^p\eta_1^q\xi_2^r\eta_2^s \frac{e^{ikr_{12}}}{r_{12}} \qquad (2)$$

eq 1 may be expressed as

$$I^m_{pqrs} = \frac{1}{i^{m+1}}\frac{\partial^{m+1}}{\partial k^{m+1}} g_{pqrs}(k)\bigg|_{k=0} \qquad (3)$$

Then, the problem is reduced to solve the integral in eq 2. For this purpose, we use the expansion of the Green function for the Helmholtz operator in prolate spheroidal coordinates:[17]

$$\frac{e^{ikr_{12}}}{r_{12}} = 4\pi ik \sum_{m,l} \frac{(2l+1)(l-m)!}{4\pi(l+m)!} S^{(1)}_{ml}\left(\frac{k}{2},\eta_1\right) S^{(1)}_{ml}\left(\frac{k}{2},\eta_2\right) e^{im(\phi_1-\phi_2)}\, je_{ml}\left(\frac{k}{2},\xi_<\right) he_{ml}\left(\frac{k}{2},\xi_>\right) \qquad (4)$$

The functions present in this expansion are the *spheroidal wave functions*.[18,19] Replacing eq 4 in eq 2 and integrating over ϕ_1 and ϕ_2, we obtain

$$g_{pqrs}(k) = 4\pi^2 ik \sum_l (2l+1) \int d^2x_1\, d^2x_2\, S^{(1)}_{0l}\left(\frac{k}{2},\eta_1\right) S^{(1)}_{0l}\left(\frac{k}{2},\eta_2\right) R^{(1)}_{0l}\left(\frac{k}{2},\xi_<\right)\left[R^{(1)}_{0l}\left(\frac{k}{2},\xi_>\right) + iR^{(2)}_{0l}\left(\frac{k}{2},\xi_>\right)\right] f_{pqrs}(\xi_1,\eta_1,\xi_2,\eta_2) \qquad (5)$$

where

$$f_{pqrs}(\xi_1,\eta_1,\xi_2,\eta_2) = \frac{e^{-(\alpha\xi_1+\beta\xi_2)}\xi_1^p\,\eta_1^q\,\xi_2^r\,\eta_2^s}{\xi_1^2-\eta_1^2} \qquad (6)$$

$$je_{0l}(c,\xi) = R^{(1)}_{0l}(c,\xi) \qquad (7)$$

$$he_{0l}(c,\xi) = R^{(1)}_{0l}(c,\xi) + iR^{(2)}_{0l}(c,\xi) \qquad (8)$$

and $d^2x_i = (\xi_i^2 - \eta_i^2)\, d\xi_i\, d\eta_i$. Further defining the two auxiliary integrals,

$$K^{(1)}_{pqrsl}(k) = \int d^2x_1\, d^2x_2\, S^{(1)}_{0l}\left(\frac{k}{2},\eta_1\right) S^{(1)}_{0l}\left(\frac{k}{2},\eta_2\right) R^{(1)}_{0l}\left(\frac{k}{2},\xi_<\right) R^{(1)}_{0l}\left(\frac{k}{2},\xi_>\right) f_{pqrs}(\xi_1,\eta_1,\xi_2,\eta_2) \qquad (9)$$

and

$$K^{(2)}_{pqrsl}(k) = \int d^2x_1\, d^2x_2\, S^{(1)}_{0l}\left(\frac{k}{2},\eta_1\right) S^{(1)}_{0l}\left(\frac{k}{2},\eta_2\right) R^{(1)}_{0l}\left(\frac{k}{2},\xi_<\right) R^{(2)}_{0l}\left(\frac{k}{2},\xi_>\right) f_{pqrs}(\xi_1,\eta_1,\xi_2,\eta_2) \qquad (10)$$

Equation 5 takes the form

$$g_{pqrs}(k) = 4\pi^2 ik \sum_{l=0}^{\infty} (2l+1)[K^{(1)}_{pqrsl}(k) + i\,K^{(2)}_{pqrsl}(k)] \qquad (11)$$

To apply eq 3, we expand eq 11 in powers of k using the power expansions of the spheroidal wave functions. A useful expansion for the angular functions of the first kind is[18]

$$S^{(1)}_{0l}(k/2, z) = d^{0l}_0(k) \sum_{j=0}^{\infty}\left[\sum_{k=b_{-2j,k_0}}^{2j}{}' \alpha^{0l}_{jk}\, P_{l+k}(z)\right]\left(\frac{k}{2}\right)^{2j} \qquad (12)$$

where $\sum'$ means that the sum is over even values of the index, $P_{l+k}(z)$ are the Legendre functions,[20] $b_{ij} = \max(i,j)$, $k_0 = l \bmod(2) - l$, and the recursive relations for the coefficients α^{0l}_{jk} are given in the appendix. In ref 18, it is also shown that $d^{0l}_0(k)$ admits the expansion

$$[d^{0l}_0(k/2)]^2 = \left[\sum_{j1=0}^{\infty}\sum_{j2=0}^{\infty}\sum_{k=-a_{2j1,2j2}}^{\alpha_{2j1,2j2}}{}' \alpha^{0l}_{j1k}\,\alpha^{0l}_{j2k}\frac{2l+1}{2l+2k+1}\left(\frac{k}{2}\right)^{2(j1+j2)}\right]^{-1} \qquad (13)$$

where $a_{i,j} = \min(i,j)$. The other special functions admit similar expansions, and we do not reproduce the details here. Then, we obtain for the auxiliary integrals

$$K^{(1)}_{pqrsl}(k) = \frac{(l!)^2}{4^{2l+1}}\left[\frac{\sum_{j=0}^{\infty}\delta_{jl}(k/2)^{2j}}{\sum_{j,i=0}^{\infty}\Delta_{ijl}(k/2)^{2(i+j)}}\right]^2\left[\frac{1}{\sum_{j,i=0}^{\infty}\tau^l_{ij}(k/2)^{2(i+j)}}\right] \sum_{j1\,j2,j3,j4=0}^{\infty}(k/2)^{2(j1+j2+j3+j4+l)}\int d^2x_1\, d^2x_2\, \gamma^{(1)}_{lj1}(\eta_1)\,\gamma^{(1)}_{lj2}(\eta_2)\,\gamma^{(1)}_{lj3}(\xi_<)\,\gamma^{(1)}_{lj4}(\xi_>)\, f_{pqrs}(\xi_1,\eta_1,\xi_2,\eta_2) \qquad (14)$$

where

$$\tau^l_{ij} = \sum_{k=-a_{2i,2j}}^{\alpha_{2i,2j}}{}' \alpha^{0l}_{ik}\,\alpha^{0l}_{jk}\frac{2l+1}{2l+2k+1} \qquad (15)$$

$$\delta_{jl} = \sum_{k=0}^{j}\frac{\alpha^{0l}_{j,-2k}}{k!\Gamma(l-k+3/2)} \qquad (16)$$

$$\Delta_{ijl} = \sum_{k=0}^{i}\sum_{m=-2j}^{2j}{}' \frac{\alpha^{0l}_{i,2k}\,\alpha^{0l}_{jm}}{k!\Gamma(-l-k+1/2)} \qquad (17)$$

and

$$\gamma^{(1)}_{lj}(z) = \sideset{}{'}\sum_{k=b_{-2j,k_0}}^{2j} \alpha^{0l}_{jk}\, P_{l+k}(z) \qquad (18)$$

Analogously, $K^{(2)}_{pqrsl}(k)$ may also be expanded as

$$K^{(2)}_{pqrsl} = -\frac{2}{k}\left[\frac{\sum\limits_{j,i=0}^{\infty}\delta_{j,l}\tilde{\delta}_{i,l}(k/2)^{2(i+j)}}{\sum\limits_{i1,i2,i3,i4=0}^{\infty}\Delta_{i2,i1,l}\tilde{\Delta}_{i4,i3,l}(k/2)^{2(i1+i2+i3+i4)}}\right]\left[\frac{1}{\sum\limits_{j,i=0}^{\infty}\tau^{l}_{ij}(k/2)^{2(i+j)}}\right]\sum_{j1,j2,j3,j4=0}^{\infty}(k/2)^{2(j1+j2+j3+j4)}\int d^2x_1\, d^2x_2\; \gamma^{(1)}_{lj1}(\eta_1)\,\gamma^{(1)}_{lj2}(\eta_2)\,\gamma^{(1)}_{lj3}(\xi_<)\,\gamma^{(2)}_{lj4}(\xi_>)\, f_{pqrs}(\xi_1,\eta_1,\xi_2,\eta_2) \qquad (19)$$

where

$$\tilde{\delta}_{jl} = \sum_{k=0}^{j}\frac{\alpha^{0l}_{j,2k}}{k!\,\Gamma(-\,l-k+1/2)} \qquad (20)$$

$$\tilde{\Delta}_{ijl} = \sum_{k=0}^{i}\sideset{}{'}\sum_{m=-2j}^{2j}\frac{\alpha^{0l}_{i,-2k}\,\alpha^{0l}_{jm}}{k!\,\Gamma(l-k+3/2)} \qquad (21)$$

and

$$\gamma^{(2)}_{lj}(z) = \sideset{}{'}\sum_{k=-2j}^{a_{k_0-2,-2j}}\tilde{\alpha}^{0l}_{jk}\, P_{-l-k-1}(z) + \sideset{}{'}\sum_{k=b_{k_0,-2j}}^{2j}\alpha^{0l}_{jk}\, Q_{k+l}(z) \qquad (22)$$

where $Q_{k+l}(z)$ are the Legendre functions[20] and the recursive expressions for the coefficients $\tilde{\alpha}^{0l}_{jk}$ are shown in the appendix.

Note that integrals present in eqs 14 and 19 do not depend on k. There are three different integrals

$$B_{m,q} = \int_{-1}^{1} P_m(\eta)\,\eta^q\, d\eta \qquad (23)$$

$$Z^{\xi}_{mnlk}(\alpha,\beta) = \int d\xi_1\, d\xi_2\, P_m(\xi_<)\, P_n(\xi_>)\, \xi_1^l\, \xi_2^k\, e^{-\alpha\xi_1}\, e^{-\beta\xi_2} \qquad (24)$$

and

$$W^{\xi}_{mnlk}(\alpha,\beta) = \int d\xi_1\, d\xi_2\, P_m(\xi_<)\, Q_n(\xi_>)\, \xi_1^l\, \xi_2^k\, e^{-\alpha\xi_1}\, e^{-\beta\xi_2} \qquad (25)$$

Integrals 23 and 25 were solved by McEachran and Cohen.[3] They obtained analytic recursion formulas sufficient to generate these integrals. For solving the integrals in eq 24, which are similar to the integrals in eq 25, we used the scheme presented in ref 3.

Now, we arrive at a final expression for $g_{pqrs}(k)$:

$$g_{pqrs}(k) = 8\pi^2 \sum_{lkentN=0}^{\infty}(2l+1)\left[\frac{i(l!)^2}{4^{2l+1}}h^{l}_{2N}\, J^{l}_{kentpqrs}\left(\frac{k}{2}\right)^{2(k+e+n+t+l+N)+1} + \tilde{h}^{l}_{2N}\, Y^{l}_{kentpqrs}\left(\frac{k}{2}\right)^{2(k+e+n+t+N)}\right] \qquad (26)$$

where

$$J^{l}_{kentpqrs} = \sideset{}{'}\sum_{k1=b_{-2k,k_0}}^{2k}\ \sideset{}{'}\sum_{k2=b_{-2e,k_0}}^{2e}\ \sideset{}{'}\sum_{k3=b_{-2n,k_0}}^{2n}\ \sideset{}{'}\sum_{k4=b_{-2t,k_0}}^{2t} A_{k1,k2,k3,k4}(l,k,e,n,t)\, B_{l+k1,\mathrm{q}}[Z^{\xi}_{l+k3,l+k4,p,r+2}(\alpha,\beta)\, B_{l+k2,s} - Z^{\xi}_{l+k3,l+k4,p,r}(\alpha,\beta)\, B_{l+k2,s+2}] \qquad (27)$$

and

$$Y^{l}_{kentpqrs} = \sideset{}{'}\sum_{k1=b_{-2k,k_0}}^{2k}\ \sideset{}{'}\sum_{k2=b_{-2e,k_0}}^{2e}\ \sideset{}{'}\sum_{k3=b_{-2n,k_0}}^{2n}\ \sideset{}{'}\sum_{k4=-2t}^{a_{k_0-2,2t}} \tilde{A}_{k1,k2,k3,k4}(l,k,e,n,t)\, B_{l+k1,q}[Z^{\xi}_{l+k3,-l-k4-1,p,r+2}(\alpha,\beta)\, B_{l+k2,s} - Z^{\xi}_{l+k3,-l-k4-1,p,r}(\alpha,\beta)\, B_{l+k2,s+2}] + \sideset{}{'}\sum_{k1=b_{-2k,k_0}}^{2k}\ \sideset{}{'}\sum_{k2=b_{-2e,k_0}}^{2e}\ \sideset{}{'}\sum_{k3=b_{-2n,k_0}}^{2n}\ \sideset{}{'}\sum_{k4=b_{-2t,k_0}}^{2t} A_{k1,k2,k3,k4}(l,k,e,n,t)\, B_{l+k1,\mathrm{q}}[W^{\xi}_{l+k3,l+k4,p,r+2}(\alpha,\beta)\, B_{l+k2,s} - W^{\xi}_{l+k3,l+k4,p,r}(\alpha,\beta)\, B_{l+k2,s+2}] \qquad (28)$$

where the coefficients A are

$$A_{k1,k2,k3,k4}(l,k,e,n,t) = \alpha^{0l}_{k,k1}\,\alpha^{0l}_{e,k2}\,\alpha^{0l}_{n,k3}\,\alpha^{0l}_{t,k4}$$
$$\tilde{A}_{k1,k2,k3,k4}(l,k,e,n,t) = \alpha^{0l}_{k,k1}\,\alpha^{0l}_{e,k2}\,\alpha^{0l}_{n,k3}\,\tilde{\alpha}^{0l}_{t,k4} \qquad (29)$$

The coefficients h^{l}_{N} and $\tilde{h}^{l}_{N}$ in eq 26 are obtained from algebraic treatment of eqs 14 and 19 by just grouping terms in powers of k.

We can see that, when we introduce eq 26 in eq 3, all the series become finite. When m in eq 1 is odd, $m + 1$ in eq 3 is even and just the second term in eq 26 survives. In this case, the sum over k, e, n, t, and N is truncated by the condition $2(k + e + n + t + N) = m + 1$. For the sum over l, we have to analyze eq 28. It is straightforward to show that $B_{mq} = 0$ for $m > q$; then, the sum over l is truncated by the condition $l + k_1 \leq q$. For even values of m, $m + 1$ is odd, just the first term in eq 26 survives, and the sum over k, e, n, t, N, and l is truncated by the condition $2(k + e + n + t + N + l) = m$.

3. Numerical Discussion

The iterative method presented in section 2 and its application to the variational calculation of the ground state of the hydrogen molecule have been tested in extensive numerical computations. It is interesting to discuss some numerical problems. The first one is the use of analytical recursion relations. It is known that these relations are numerically very unstable, to the extreme that one or two significant

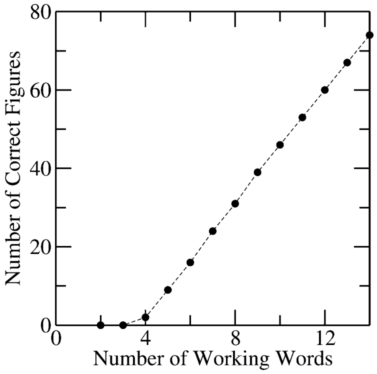

Figure 1. Number of correct figures against number of working words for the integral I^m_{pqrs} with $\alpha = \beta = 1.2$, $p = 12$, $q = 12$, $r = 10$, $s = 10$, and $m = 7$.

figures may be lost by iteration. To avoid this problem, we wrote all our codes using MPFUN, a multiprecision Fortran-90 package,[21] which allows for working with an arbitrary precision. MPFUN was successfully applied to high-precision calculations in quantum few-body systems.[22,23] In this work, we made our calculations with 100 figures, in contrast to the maximum 32 figures that allows quadruple precision in standard Fortran-90.

To check the numerical stability of our method, we evaluated one of the typical integrals in eq 1, I^m_{pqrs}, with different accuracy levels. In particular, in Figure 1, we show the number of correct figures obtained for the integral I^m_{pqrs} with $p = 12$, $q = 12$, $r = 10$, $s = 10$, and $m = 7$ as a function of the used accuracy level in words (one word is equal to seven figures).[21] The graphic is almost independent of the value of m, and the numerical error grows with p, q, r, and s; therefore, we chose their maximum values used in our calculations in section 4. We varied the accuracy from 1 to 14 words ($\simeq$100 digits), and we compared it with the result obtained using 42 ($\simeq$300 digits), which is considered to have more than 100 correct figures. It is interesting to note that no correct digits are obtained with three-word calculations. This means that it is not possible to use standard double precision Fortran (16 figures). We get only nine correct digits with five words ($\simeq$35 figures); therefore, no reliable results may be obtained using standard quadruple precision (32 figures). In Table 1, integrals with 70 significant figures are presented.

Once the integrals are calculated, they are used in Ritz variational calculations (see section 4). The James–Coolidge basis set is not orthogonal; for this reason, it is necessary to solve a generalized eigenvalue problem.[24] The solution of a linear system with ill-conditioned matrices produces a significant loss of numerical accuracy which has to be added to the accuracy lost in the first step of the work (integrals evaluation). In our case, all the matrices involved in the generalized eigenvalue problem are extremely ill-conditioned. The overlap matrix is a positive definite matrix, but it may become nonpositive as a result of numerical accuracy problems. To avoid this, it is necessary to compute the matrix elements with great accuracy. Frolov and Bailey,[22] in the study of three body systems, ensure that they needed to work with 84–100 digits in order to produce final results with 30 correct figures. In this work, we started the calculations with 100 figures to obtain all the matrix elements with 70 correct figures. The generalized eigenvalue problem is solved applying the *Cholesky decomposition* to the overlap matrix in order to recover a standard symmetric eigenvalue problem.[24] This transformation was also done with the MPFUN package. Although the CPU time for high-precision calculation is expected to scale as a power of the number of working words, the integrals were evaluated in a reasonable time on a personal computer. The numerical evaluation of all the integrals used in section 4 takes about 81 min and the Cholesky decomposition 155 min on a 3 GHz Pentium 4 processor.

The transformed matrix elements have more than 16 correct figures. Then, the last step, the eigenvalues determination, is performed in standard double-precision Fortran-90.

4. The Hydrogen Molecule

As an application of the method described in section 2, we calculate the ground-state energy and equilibrium radii of the hydrogen molecule in the Born–Oppenheimer approximation. The Hamiltonian of this system, in atomic units, is

$$H = \sum_{i=1}^{2}\left(-\frac{1}{2}\nabla_i^2 - \frac{1}{|\vec{r}_i - \vec{R}/2|} - \frac{1}{|\vec{r}_i + \vec{R}/2|}\right) + \frac{1}{r_{12}} + \frac{1}{R} \qquad (30)$$

To apply the Ritz variational principle, we need to evaluate where

$$H_{ij} = \langle\phi_i|\, H|\phi_j\rangle \qquad S_{ij} = \langle\phi_i|\phi_j\rangle \qquad (31)$$

$$\phi_n = C\, \mathrm{e}^{-\alpha(\xi_1+\xi_2)}\, (\xi_1^{p_n}\, \eta_1^{q_n}\, \xi_2^{r_n}\, \eta_2^{s_n} + \xi_1^{r_n}\, \eta_1^{s_n}\, \xi_2^{p_n}\, \eta_2^{q_n}) r_{12}^{m_n} \qquad (32)$$

Here, C is the normalization constant. It is obvious that the ground-state wave function has to be invariant under inversion with respect to the plane of symmetry of the molecule. As a result, we have the restriction that $q_n + s_n$ must be even. To obtain the ground-state energy of the system, we have to find the lowest root of

$$\mathrm{Det}(\mathbf{H} - E\mathbf{S}) = 0 \qquad (33)$$

An optimization of the parameter α was done with a 1710-term wave function. The optimal value obtained was $\alpha = 1.2$.

In this work, the quantum numbers of the basis function eq 32 are allowed to take values from 0 to 5. We calculated the ground-state energy of the hydrogen molecule for different values of the internuclear distance R with the 2052-term wave function.

We obtained for the equilibrium distance $R_{\mathrm{eq}} = 1.401\,08$ and for the correspondent ground-state energy $E_0(R_{\mathrm{eq}}) = -1.174\,475\,930\,2$ au. In Table 2, we show the energy for $R = 1.4$ as we increase the correlation power m. The case $m = 0$ is the noncorrelated approximation.[3] The values for $R = 1.4$ were calculated for comparison with other results available in the literature. Our value for the ground-state energy of the hydrogen molecule for $R = 1.4$ is lower than the values reported by Kolos, using a modified James–Coolidge expansion with two variational parameters,[4] and

Table 1. Integrals I^{m}_{pqrs} for $\alpha = \beta = 1.2$ and $p = 12$, $q = 12$, $r = 10$, $s = 10$, $m = -1$ to 10

m	$I^{m}_{12,12,10,10}$ ($\alpha = \beta = 1.2$)
-1	$1.5730011931381573753421872778320560951340964616442301882419969435564 88 \times 10^{7}$
0	$3.176330368272650430058801479662460509518556660306229387659127078650 55 \times 10^{7}$
1	$1.0907425878709640479558339835521415441789883893975196907765468962825 91 \times 10^{8}$
2	$5.0217247073759871252844425511005293266677403997579240347658890065083 10 \times 10^{8}$
3	$2.6581747756897666128320296984127588931184120435589314461812544653896 13 \times 10^{9}$
4	$1.5154267652614192998335917564708862152320649131576927145697104115727 81 \times 10^{10}$
5	$9.0775171286533976397279142053571939917643899700670074325487466537416 53 \times 10^{10}$
6	$5.6573566442446294189586605878509108683345795646202298539057885084897 61 \times 10^{11}$
7	$3.6520942228007702270629306356899617837451678586386256605667138555517 16 \times 10^{12}$
8	$2.4361670866937773363645542254547871718278943746804922945577684733414 09 \times 10^{13}$
9	$1.6765976960284047474425478218684176109051587564583701061378539553662 83 \times 10^{14}$
10	$1.1890312344203270237513163546801056253197226594681086990244100048783 11 \times 10^{15}$

Table 2. Variational Ground-State Energy for the Hydrogen Molecule with Maximum Values $p = 5$, $q = 5$, $r = 5$, and $s = 5$

m	$E(R = 1.4)$
0	−1.161 482 984 33
1	−1.174 435 130 87
2	−1.174 475 155 80
3	−1.174 475 700 00
4	−1.174 475 711 87
5	−1.174 475 713 00
W. Kolos (1994)[4]	−1.174 475 686
H. Nakatsuji (2004)[5]	−1.174 475 703

by Nakatsuji, using a modified James−Coolidge expansion allowing negatives values of (p_n, r_n) in the basis function eq 32.

5. Conclusions

The main contribution of this paper is a new analytical method for the evaluation of the James−Coolidge two-center, two-electron integrals. The method is based on the standard expansion for the free Green function for the Helmholtz operator in spheroidal wave functions[17] and uses the new expressions obtained by Falloon for those special functions.[18,19]

The formulas presented have been successfully tested in numerical calculations for the Born−Oppenheimer hydrogen molecule ground-state energy. To obtain the Hamiltonian matrix elements correct up to 16 decimal places, we used the MPFUN package[21] with roughly 100 digits in the recurrence relations for the integrals and Cholesky decomposition of the overlap matrix.

The method presented in this work is appropriate for high-precision variational calculations of bound states of other two-center, two-electron Hamiltonians. As a relevant application, the existence of dipole dianions will be addressed in a forthcoming paper.

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Appendix

Recurrence Relations for the Coefficients. Here, we present the recurrence relation for the coefficients α^{0l}_{jk} and $\tilde{\alpha}^{0l}_{jk}$ taken from ref 18, which are

$$\alpha^{0l}_{jk} = \frac{1}{(l+k)(l+k+1) - l^{0l}_{0}}\Big[\sum_{i=0}^{j-1} l^{0l}_{i+1}\,\alpha^{0l}_{j-i-1,k} - (a_{0lk}\alpha^{0l}_{j-1,k+2} + \beta_{0lk}\alpha^{0l}_{j-1,k} + \gamma_{0lk}\alpha^{0l}_{j-1,k-2})\Big] \quad (34)$$

$$a_{0lk} = \frac{(l+k+1)(l+k+2)}{(2l+2k+3)(2l+2k+5)} \quad (35)$$

$$\beta_{0lk} = \frac{1}{2}\left(1 + \frac{1}{(2l+2k-1)(2l+2k+3)}\right) \quad (36)$$

$$\gamma_{0lk} = \frac{(l+k)(l+k-1)}{(2l+2k-3)(2l+2k-1)} \quad (37)$$

$$l^{0l}_{0} = l(l+1), \qquad l^{0l}_{1} = \beta_{0l0}, \qquad l^{0l}_{j} = a_{0l0}\alpha^{0l}_{j-1,2} + \gamma_{0l0}\alpha^{0l}_{j-1,-2} \qquad j \geq 2 \quad (38)$$

$$\tilde{\alpha}^{0l}_{jk} = \frac{1}{(l+k)(l+k+1) - l^{0l}_{0}}\Big[\sum_{i=0}^{j-1} l^{0l}_{i+1}\,\tilde{\alpha}^{0l}_{j-i-1,k} - (\tilde{a}_{0l}\alpha^{0l}_{j-1,k+2} + \beta_{0lk}\tilde{\alpha}^{0l}_{j-1,k} + \gamma_{0lk}\tilde{\alpha}^{0l}_{j-1,k-2})\Big] \quad (39)$$

for $k = k_0 - 2$ and

$$\tilde{\alpha}^{0l}_{jk} = \frac{1}{(l+k)(l+k+1) - l^{0l}_{0}}\Big[\sum_{i=0}^{j-1} l^{0l}_{i+1}\,\tilde{\alpha}^{0l}_{j-i-1,k} - (a_{0l}\alpha^{0l}_{j-1,k+2} + \beta_{0lk}\tilde{\alpha}^{0l}_{j-1,k} + \gamma_{0lk}\tilde{\alpha}^{0l}_{j-1,k-2})\Big] \quad (40)$$

for $k = k_0 - 4$, $k_0 - 6$, and so forth, and $\tilde{a}_{0l} = 1$ for even l values, and $\tilde{a}_{0l} = {}^{1}/_{3}$ for odd l values.

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