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 Coolidge1 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 atom15 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
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:

\[ P_{pqrs}^m = \frac{(2\pi)^6}{\mathcal{R}} \int d^3x_1 \ d^3x_2 \ \frac{e^{-(\alpha_1^2+\beta_2^2)}}{\xi_1^2-\eta_1^2} \ \theta^{re}(\xi_1)\theta^{re}(\eta_2) S_{12}^m (\xi, \eta_1, \eta_2) \]  
(1)

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

Introducing the auxiliary integral

\[ g_{pqrs}(k) = \frac{(2\pi)^6}{\mathcal{R}} \int d^3x_1 \ d^3x_2 \ \frac{e^{-\alpha_1^2-\beta_2^2}}{\xi_1^2-\eta_1^2} \ \theta^{kr}(\xi_1)\theta^{kr}(\eta_2) S_{12}^m (\xi, \eta_1, \eta_2) \]  
(2)

eq 1 may be expressed as

\[ P_{pqrs}^m = \frac{1}{m+1} \frac{\partial^{m+1}}{\partial k^{m+1}} g_{pqrs}(k) \bigg|_{k=0} \]  
(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:

\[ e^{ikr_{12}} = 4\pi ik \sum_{m \in \mathbb{Z}} (2l + 1)(l - m)! \frac{S_{12}^l(k \xi_1) S_{12}^l(k \xi_2) e^{i(m\phi_1 - m\phi_2)}}{4\pi(l + m)!} \]  
(4)

The functions present in this expansion are the spheroidal wave functions. Replacing eq 4 in eq 2 and integrating over \(\phi_1\) and \(\phi_2\), we obtain

\[ g_{pqrs}(k) = 4\pi^2 i k \sum_l (2l + 1) \int d^3x_1 \ d^3x_2 S_{12}^l \left( \frac{k}{2} \xi_1 \right) S_{12}^l \left( \frac{k}{2} \xi_2 \right) \]  
(5)

\[ R_{kl}^{(1)}(\xi, \eta_1, \eta_2) \]  
(6)

\[ j e^{ik(c, \xi)} = R_{kl}^{(1)}(c, \xi) \]  
(7)

\[ h e^{ik(c, \xi)} = R_{kl}^{(2)}(c, \xi) + i R_{kl}^{(3)}(c, \xi) \]  
(8)

and \(d^3x = (\xi^2 - \eta^2) \ \xi \ \xi \ \eta d\xi\). Further defining the two auxiliary integrals,

\[ K_{pqrs}^{(1)}(k) = \int d^3x_1 d^3x_2 S_{12}^l \left( \frac{k}{2} \xi_1 \right) R_{kl}^{(1)} \left( \frac{k}{2} \xi_2 \right) \]  
(9)

and

\[ K_{pqrs}^{(2)}(k) = \int d^3x_1 d^3x_2 S_{12}^l \left( \frac{k}{2} \xi_1 \right) R_{kl}^{(2)} \left( \frac{k}{2} \xi_2 \right) \]  
(10)

Equation 5 takes the form

\[ g_{pqrs}(k) = 4\pi^2 i k \sum_{l=0}^{\infty} [(K_{pqrs}^{(1)}(k) + i K_{pqrs}^{(2)}(k))] \]  
(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

\[ S_{12}^l(k/2, z) = d_0^l(k) \sum_{j=0}^{\infty} \sum_{a_0, a_{1,2}} a_{j,k} a_{j,2} \left( \frac{k}{2} \right)^{2j} \]  
(12)

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

\[ K_{pqrs}^{(1)}(k) = \left( \frac{l!}{2} \right) \int \sum_{j=0}^{\infty} \delta_{j,l} (k/2)^{2j} \sum_{j=0}^{\infty} t_{l,j} (k/2)^{2j+l} \]  
(13)

where

\[ t_{l,j} = \sum_{a_0, a_{1,2}} a_{j,k} a_{j,2} \left( \frac{k}{2} \right)^{2j+1} \]  
(14)

and

\[ \delta_{j,l} = \sum_{k=0}^{\infty} \delta_{j,k} \Gamma(l + k - 3/2) \]  
(15)

\[ \Delta_{ij} = \sum_{k=0}^{\infty} \sum_{m=-2}^{2} \delta_{j,k} \delta_{m,l} \]  
(16)
\[
\gamma_{ij}^{(1)}(z) = \sum_{k=0}^{2i} \alpha_{jk}^0 P_{2k}(z) \tag{18}
\]

Analogously, \(K_{\text{ppsr}l}^{(2)}(k)\) may also be expanded as
\[
K_{\text{ppsr}l}^{(2)} = -\frac{2}{k} \sum_{j=0}^{\infty} \sum_{l,j=0}^{\infty} e^{(l+j/2)^2} \left[ \sum_{j=0}^{\infty} \sum_{l,j=0}^{\infty} G_{l,j} \right] e^{(l+j/2)^2} \left[ \sum_{j=0}^{\infty} \sum_{l,j=0}^{\infty} G_{l,j} \right] \int d^2x_1 d^2x_2
\]
\[
\gamma_{ij}^{(2)}(\eta_1) \gamma_{ij}^{(2)}(\eta_2) \gamma_{ij}^{(2)}(\xi_1) \gamma_{ij}^{(2)}(\xi_2) f_{\text{ppsr}}(\xi_1, \eta_1, \xi_2, \eta_2) \tag{21}
\]

where
\[
\delta_{ij} = \sum_{k=0}^{\infty} \frac{\alpha_{jk}^0}{k!} \tag{20}
\]
\[
\Delta_{ij} = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \frac{\alpha_{jk}^0 \alpha_{il}^0}{k!} \tag{21}
\]

and
\[
\gamma_{ij}^{(2)}(z) = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \alpha_{jk}^0 P_{2k}(z) + \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \alpha_{jk}^0 Q_{k+i}(z) \tag{22}
\]

where \(Q_{k+i}(z)\) are the Legendre functions and the recursive expressions for the coefficients \(\alpha_{jk}^0\) are shown in the appendix.

Now, we arrive at a final expression for \(g_{\text{ppsr}}(k)\):
\[
g_{\text{ppsr}}(k) = 8\pi^2 \sum_{k=0}^{\infty} (2l + 1) \left[ \frac{i(l+1)^2}{4} \right] \sum_{l=0}^{\infty} h_{2N}^{(k)l} f_{\text{ppsr}}(k/2)^{2(k+e+n+r+t+N)+1} \]

where
\[
f_{\text{ppsr}}(k) = \sum_{k=1}^{\infty} \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} A_{k\ell,m,n,t} B_{k\ell,m,n,t} Z_{k\ell,m,n,t}\tag{27}
\]

and
\[
\gamma_{ij}^{(2)}(\eta_1) \gamma_{ij}^{(2)}(\eta_2) \gamma_{ij}^{(2)}(\xi_1) \gamma_{ij}^{(2)}(\xi_2) f_{\text{ppsr}}(\xi_1, \eta_1, \xi_2, \eta_2) \tag{21}
\]

where the coefficients \(A\) are
\[
A_{k\ell,m,n,t} = \sum_{k=1}^{\infty} \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} A_{k\ell,m,n,t} B_{k\ell,m,n,t} Z_{k\ell,m,n,t}\tag{28}
\]

The coefficients \(h_{2N}^{(k)l}\) and \(h_{2N}^{(k)l}\) 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 \(B_{2q} = 0\) 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 \(k, e, n, t,\) and \(N\) 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
of the used accuracy level in words (one word is equal
to 5 figures). In Table 1, integrals with 70 significant figures are
obtained using 42 (seven-word) calculations. The James
Coolidge expansion with two variational parameters, 4 and
35 figures); therefore, no reliable results
are obtained with three-word calculations.

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. 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,\textsuperscript{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.\textsuperscript{23} 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 determina-
tion, 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 approxi-
mation. The Hamiltonian of this system, in atomic units, is

\[
H = \sum_{i=1}^{2} \left( -\frac{1}{2} \nabla_i^2 - \frac{1}{|\mathbf{r}_i - \mathbf{R}|} - \frac{1}{|\mathbf{r}_i + \mathbf{R}|} \right) + \frac{1}{\mathbf{r}_{12}} + \frac{1}{R} \tag{30}
\]

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

\[
H_{ij} = \langle \phi_i | H | \phi_j \rangle \quad S_{ij} = \langle \phi_i | \phi_j \rangle \tag{31}
\]

\[
\phi_n = C e^{-\alpha(|\mathbf{r}|+2)} \left( \frac{2}{\beta} \frac{\partial}{\partial |\mathbf{r}|} \right)^2 (\xi_{1n} \eta_{2n}^* \xi_{2n} \eta_{1n}^* + \xi_{2n}^* \eta_{1n} \xi_{1n}^* \eta_{2n}^*) \tag{32}
\]

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

\[
\text{Det}(H - ES) = 0 \tag{33}
\]

An optimization of the parameter \( \alpha \) 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 \( R_{eq} = 1.401 \) 08
and for the correspondent ground-state energy
\( E_0(R_{eq}) = -1.174 \) 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.\textsuperscript{24}\textsuperscript{25}
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,\textsuperscript{24} and
Table 1. Integrals $f_{\text{Jp}}^{\text{M}}$ for $\alpha = \beta = 1.2$ and $p = 12$, $q = 12$, $r = 10$, $s = 10$, $m = -1$ to 10

<table>
<thead>
<tr>
<th>$m$</th>
<th>$f_{\text{Jp}}^{\text{M}}$ ($\alpha = \beta = 1.2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>1.573011931381573542187277832056095134904964164423018824199694356488 $\times 10^7$</td>
</tr>
<tr>
<td>1</td>
<td>3.1763303682726504300580801479662460509518556603062932987675912707865055 $\times 10^8$</td>
</tr>
<tr>
<td>0</td>
<td>1.0907425587809404795583993521415441788838939751966077654689282591 $\times 10^8$</td>
</tr>
<tr>
<td>2</td>
<td>5.02172470737598712528444255110052932667740399759724037568580906508301 $\times 10^8$</td>
</tr>
<tr>
<td>10</td>
<td>2.6581747756897661283202969841275859311841204558931446181254465389613 $\times 10^8$</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>$m$</th>
<th>$E(R = 1.4)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-1.161 482 984 33</td>
</tr>
<tr>
<td>1</td>
<td>-1.174 435 130 87</td>
</tr>
<tr>
<td>2</td>
<td>-1.174 475 155 80</td>
</tr>
<tr>
<td>3</td>
<td>-1.174 475 700 00</td>
</tr>
<tr>
<td>4</td>
<td>-1.174 475 711 87</td>
</tr>
<tr>
<td>5</td>
<td>-1.174 475 713 00</td>
</tr>
</tbody>
</table>

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 diatomic 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 $a_{jk}^{0\ell}$ and $a_{jk}^{0\ell}$ taken from ref 18, which are

$$a_{jk}^{0\ell} = \frac{1}{(l+k)(l+k+1) - \rho_{0\ell}^{0\ell}} \left[ \sum_{i=1}^{j-1} a_{i,j-1,i,k}^{0\ell} + \beta_{0\ell}^{0\ell} a_{i,j-1,i,k}^{0\ell} + \gamma_{0\ell}^{0\ell} a_{i,j-2,i,k}^{0\ell} \right]$$

$$a_{jk}^{0\ell} = \frac{1}{(l+k+1)(l+k+2)} \left[ \sum_{i=1}^{j-1} a_{i,j-2,i,k}^{0\ell} \right]$$

$$a_{jk}^{0\ell} = \beta_{0\ell}^{0\ell} \left[ \sum_{i=1}^{j-1} a_{i,j-2,i,k}^{0\ell} \right]$$

$$a_{jk}^{0\ell} = \gamma_{0\ell}^{0\ell} \left[ \sum_{i=1}^{j-1} a_{i,j-2,i,k}^{0\ell} \right]$$

for $k = 0$ and

$$a_{jk}^{0\ell} = \frac{1}{(l+k)(l+k+1) - \rho_{0\ell}^{0\ell}} \left[ \sum_{i=1}^{j-1} a_{i,j-1,i,k}^{0\ell} \right]$$

$$a_{jk}^{0\ell} = \beta_{0\ell}^{0\ell} \left[ \sum_{i=1}^{j-1} a_{i,j-1,i,k}^{0\ell} \right]$$

$$a_{jk}^{0\ell} = \gamma_{0\ell}^{0\ell} \left[ \sum_{i=1}^{j-1} a_{i,j-1,i,k}^{0\ell} \right]$$

for $k = 0$, $k = 6$, and so forth, and $a_{0\ell}^{0\ell} = 1$ for even $l$ values, and $a_{0\ell}^{0\ell} = \frac{1}{l}$ for odd $l$ values.

References

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