Evaluation of Two Center Two Electron Integrals

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Abstract

We present a new analytic treatment of two electron integrals over two centre 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 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, 2, 3, 4, 5]. Two electron addition to closed-shell neutral polar molecules may be also 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 on the study of the possible existence of such dipole-bound dianions [6, 7, 8, 9]. The study of this kind of weakly bound states represent an interesting field of research. For these states the energy is non analytical as a function of the dipolar moment and a bound-state could not exist at the threshold energy, therefore they might be a good candidate to be a halo state [10]. Technical problems appear when standard approximations like 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 [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 letter 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.
Two Electron Integrals Over Two-centre 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]

\[ I_{pqrs}^m = \int d^3x_1 d^3x_2 \frac{e^{-(\alpha \xi_1 + \beta \xi_2)}}{\xi_1^2 - \eta_1^2} \xi_1^p \eta_1^q \xi_2^r \eta_2^s \xi_1^s \xi_2^m, \]  

(1)

where the integral is expressed in usual prolate spheroidal coordinates \((\xi, \eta, \phi)\) [17]. \(\phi\) 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 centres, \(R\) represents the distance between centres, \(r_{12}\) is the interelectronic distance, and \(m \geq -1\).

Introducing the auxiliary integral

\[ g_{pqrs}(k) = \int d^3x_1 d^3x_2 \frac{e^{-(\alpha \xi_1 + \beta \xi_2)}}{\xi_1^2 - \eta_1^2} \xi_1^p \eta_1^q \xi_2^r \eta_2^s e^{ikr_{12}} \xi_1^s \xi_2^m, \]  

(2)

Eq. (1) may be expressed as

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

(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 [17]:

\[ e^{ikr_{12}} / r_{12} = 4\pi i k \sum_{m,l} \frac{(2l + 1)(l - m)!}{4\pi (l + m)!} c_{ml}^{(1)}(k/2, \eta_1) c_{ml}^{(1)}(k/2, \eta_2) e^{im(\phi_1 - \phi_2)} j e_{ml}(k/2, \xi_1, \xi_2) h e_{ml}(k/2, \xi_1, \xi_2). \]  

(4)

The functions present in this expansion are the spheroidal wave functions [18, 19]. Replacing Eq. (4) in Eq. (2) and integrating over \(\phi_1\) and \(\phi_2\) we obtain

\[ g_{pqrs}(k) = 4\pi^2 i k \sum_l (2l + 1) \int d^2x_1 d^2x_2 c_{ol}^{(1)}(k/2, \eta_1) c_{ol}^{(1)}(k/2, \eta_2) R_{ol}^{(1)}(k/2, \xi_1, \xi_2) R_{ol}^{(1)}(k/2, \xi_1, \xi_2) f_{pqrs}(\xi_1, \eta_1, \xi_2, \eta_2), \]  

(5)

where

\[ f_{pqrs}(\xi_1, \eta_1, \xi_2, \eta_2) = \frac{e^{-(\alpha \xi_1 + \beta \xi_2)}}{\xi_1^2 - \eta_1^2} \xi_1^p \eta_1^q \xi_2^r \eta_2^s \xi_1^s \xi_2^m. \]  

(6)

\[ j e_{ol}(c, \xi) = R_{ol}^{(1)}(c, \xi), \]  

(7)

\[ h e_{ol}(c, \xi) = R_{ol}^{(1)}(c, \xi) + i R_{ol}^{(2)}(c, \xi), \]  

(8)

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

3
\begin{align*}
K_{pqrs}^{(1)}(k) &= \int d^2x_1 d^2x_2 S_{0l}^{(1)}(\frac{k}{2}, \eta_1) S_{0l}^{(1)}(\frac{k}{2}, \eta_2) \\
R_{0l}^{(1)}(\frac{k}{2}, \xi_<) R_{0l}^{(1)}(\frac{k}{2}, \xi_>) f_{pqrs}(\xi_1, \eta_1, \xi_2, \eta_2) 
\end{align*}

and

\begin{align*}
K_{pqrs}^{(2)}(k) &= \int d^2x_1 d^2x_2 S_{0l}^{(1)}(\frac{k}{2}, \eta_1) S_{0l}^{(1)}(\frac{k}{2}, \eta_2) \\
R_{0l}^{(1)}(\frac{k}{2}, \xi_<) R_{0l}^{(2)}(\frac{k}{2}, \xi_>) f_{pqrs}(\xi_1, \eta_1, \xi_2, \eta_2) .
\end{align*}

Eq. (5) takes the form

\begin{equation}
g_{pqrs}(k) = 4\pi^2 ik \sum_{l=0}^{\infty} (2l + 1) (K_{pqrs}^{(1)}(k) + i K_{pqrs}^{(2)}(k)) .
\end{equation}

In order 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]

\begin{equation}
S_{0l}^{(1)}(k/2, z) = d_{0l}^{(1)}(k) \sum_{j=0}^{2} \sum'_{k=b_{-2j}, k_0} \alpha_{jk}^{(1)} P_{l+k}(z) \left( \frac{k}{2} \right)^{2j} ,
\end{equation}

where \( \sum' \) means that the sum is over even values of the index, \( P_{l+k}(z) \) are the Legendre functions [20], \( b_{ij} = \max(i, j) \), \( k_0 = l \mod(2) - l \) and the recursive relations for the coefficients \( \alpha_{jk}^{(1)} \) are given in the appendix. In ref. [18] it is also shown that \( d_{0l}^{(1)}(k) \) admits the expansion

\begin{equation}
(d_{0l}^{(1)}(k/2))^2 = \left( \sum_{j=0}^{\infty} \sum_{j'=-2j, j=0}^{\infty} \alpha_{j1}^{(1)} \alpha_{j2}^{(1)} \alpha_{j3}^{(1)} \alpha_{j4}^{(1)} \frac{2l + 1}{2l + 2k + 1} \left( \frac{k}{2} \right)^{2(l+j_1+j_2)} \right)^{-1} ,
\end{equation}

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

\begin{align*}
K_{pqrs}^{(1)}(k) &= \frac{(1l)^2}{4^{2l+1}} \left( \sum_{j=0}^{\infty} \delta_{jl}(k/2)^{2j} \right) \left( \sum_{j=0}^{\infty} \Delta_{jj}(k/2)^{2(i+j)} \right)^2 \\
&\quad \sum_{j_1,j_2,j_3,j_4=0}^{\infty} (k/2)^{2(j_1+j_2+j_3+j_4+l)} \int d^2x_1 d^2x_2 \gamma_{i_1 j_1}^{(1)}(\eta_1) \gamma_{i_2 j_2}^{(1)}(\eta_2) \gamma_{i_3 j_3}^{(1)}(\xi_<) \gamma_{i_4 j_4}^{(1)}(\xi_>) f_{pqrs}(\xi_1, \eta_1, \xi_2, \eta_2) .
\end{align*}
where

\[ \tau_{ij}^l = \sum_{k=-a_{2i,2j}}^{a_{2i,2j}} \alpha_{ik}^l \alpha_{jk}^l \frac{2l + 1}{2l + 2k + 1} \]  

(15)

\[ \delta_{jl} = \sum_{k=0}^{j} \frac{\alpha_{j-2k}^l}{k! \Gamma(l + k + 3/2)} \]  

(16)

\[ \Delta_{ijl} = \sum_{k=0}^{i} \sum_{m=-2j}^{2j} \frac{\alpha_{m,2k}^l \alpha_{jm}^l}{k! \Gamma(l + k + 1/2)} \]  

(17)

and

\[ \gamma_{ij}^{(1)}(z) = \sum_{k=b_{-2j,2j}}^{2j} \alpha_{jk}^l P_{l+k}(z) \]  

(18)

analogously, \( K_{pqrs}^{(2)}(k) \) may also be expanded as

\[ K_{pqrs}^{(2)} = -\frac{2}{k} \left( \sum_{j=0}^{\infty} \sum_{i=1}^{\infty} \delta_{jl} \Delta_{ijl} \left( \frac{k}{2} \right)^{2(i+j)} \right) \left( \sum_{j=0}^{\infty} \tau_{ij}^l \left( \frac{k}{2} \right)^{2(i+j)} \right)^{-1} \]  

\[ \sum_{j1,j2,j3,j4=0}^{\infty} (k/2)^{2(j1+j2+j3+j4)} \int d^2x_1 d^2x_2 \gamma_{l1}^{(1)}(\eta_1) \gamma_{l2}^{(1)}(\eta_2) \gamma_{l3}^{(1)}(\xi_<) \gamma_{l4}^{(2)}(\xi_>) f_{pqrs}(\xi_1, \eta_1, \xi_2, \eta_2), \]  

(19)

where

\[ \tilde{\delta}_{jl} = \sum_{k=0}^{j} \frac{\alpha_{j-2k}^l}{k! \Gamma(-l + k + 1/2)} \]  

(20)

\[ \tilde{\Delta}_{ijl} = \sum_{k=0}^{i} \sum_{m=-2j}^{2j} \frac{\alpha_{m,2k}^l \alpha_{jm}^l}{k! \Gamma(-l + k + 3/2)} \]  

(21)

and

\[ \gamma_{ij}^{(2)}(z) = \sum_{k=-2j}^{a_{2j,-2j}} \tilde{\alpha}_{jk}^l P_{l-k-1}(z) + \sum_{k=b_{-2j,2j}}^{2j} \alpha_{jk}^l Q_{k+l}(z), \]  

(22)

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

Note that integrals present in Eqs. (14) and (19) do not depend on \( k \). There are three different integrals

\[ B_{m,q} = \int_{-1}^{1} P_m(\eta) \eta^q d\eta \]  

(23)
\[ Z_{mnlt}^{\xi}(\alpha, \beta) = \int d\xi_1 d\xi_2 P_m(\xi_1) P_n(\xi_2) \xi_1^l \xi_2^k e^{-\alpha \xi_1 - \beta \xi_2} \] 

(24)

and

\[ W_{mnlt}^{\xi}(\alpha, \beta) = \int d\xi_1 d\xi_2 P_m(\xi_1) Q_n(\xi_2) \xi_1^l \xi_2^k e^{-\alpha \xi_1 - \beta \xi_2} \] 

(25)

Integrals (23) and (25) were solved by Mc Eachran and Cohen [3]. They obtained analytic recursion formulae 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 to a final expression for \( g_{pqrs}(k) \)

\[
g_{pqrs}(k) = 8\pi^2 \sum_{l \text{ even} N=0}^{\infty} (2l + 1) \left[ \frac{i(l)!^2}{4^{2l+1}} h_{2N}^l J_{k N}^{l, pqrs} \left( \frac{k}{2} \right)^{2(k+m+n+t+2N)+1} + \right. 
\]

\[
\tilde{h}_{2N}^l Y_{k N}^{l, pqrs} \left( \frac{k}{2} \right)^{(2(k+m+n+t+2N)} \right] 
\]

(26)

where

\[
J_{k N}^{l, pqrs} = \sum_{l1=b-2k, l0}^{2k} \sum_{l2=b-2e, l0}^{2e} \sum_{l3=b-2m, l0}^{2m} \sum_{l4=b-2t, l0}^{2t} \alpha_{l1,l2,l3,l4} A_{k1,k2,k3,k4}(l, k, e, n, t) B_{l+k1,q} 
\]

\[
\left[ Z_{l+k3,l+k4,p,r+2}^{\xi}(\alpha, \beta) B_{l+k2,s} - Z_{l+k3,l+k4,p,r}(\alpha, \beta) B_{l+k2,s+2} \right] ; 
\]

(27)

and

\[
Y_{k N}^{l, pqrs} = \sum_{l1=b-2k, l0}^{2k} \sum_{l2=b-2e, l0}^{2e} \sum_{l3=b-2m, l0}^{2m} \sum_{l4=b-2t, l0}^{2t} \alpha_{l1,l2,l3,l4} A_{k1,k2,k3,k4}(l, k, e, n, t) B_{l+k1,q} 
\]

\[
\left[ Z_{l+k3,-l+k4-1,p,r+2}^{\xi}(\alpha, \beta) B_{l+k2,s} - Z_{l+k3,-l+k4-1,p,r}(\alpha, \beta) B_{l+k2,s+2} \right] + 
\]

\[
\sum_{l1=b-2k, l0}^{2k} \sum_{l2=b-2e, l0}^{2e} \sum_{l3=b-2m, l0}^{2m} \sum_{l4=b-2t, l0}^{2t} \alpha_{l1,l2,l3,l4} A_{k1,k2,k3,k4}(l, k, e, n, t) B_{l+k1,q} 
\]

\[
\left[ W_{l+k3,l+k4,p,r+2}^{\xi}(\alpha, \beta) B_{l+k2,s} - W_{l+k3,l+k4,p,r}(\alpha, \beta) B_{l+k2,s+2} \right] , 
\]

(28)

where the coefficients \( A \) are

\[
A_{k1,k2,k3,k4}(l, k, e, n, t) = \alpha_{l1,l2,l3,l4}^{0l} \alpha_{e,k2}^{0l} \alpha_{n,k3}^{0l} \alpha_{t,k4}^{0l} 
\]

\[
\tilde{A}_{k1,k2,k3,k4}(l, k, e, n, t) = \alpha_{l1,l2,l3,l4}^{0l} \alpha_{e,k2}^{0l} \alpha_{n,k3}^{0l} \tilde{\alpha}_{t,k4}^{0l} . 
\]

(29)

The coefficients \( h_{N}^{l} \) and \( \tilde{h}_{N}^{l} \) 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 (26) survives. In this case the sum over $k, e, n, t, N$ 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 and just the first term in Eq. (26) survives and the sum over $k, e, n, t, N, l$ 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 figures may be lost by iteration. To avoid this problem we wrote all our codes using MPFUN, a multi-precision Fortran-90 package [21], that allows to work 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 with the maximum 32 figures that allows quadruple precision in standard Fortran-90.

In order to check the numerical stability of our method we evaluated one of the typical integrals in Eq. (1), $I_{pqrs}^m$, with different accuracy levels. In particular, in figure 1 we show the number of correct figures obtained for the integral $I_{pqrs}^m$ with $p = 12, q = 12, r = 10, s = 10, m = 7$ 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 $p, q, r, s$, 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 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 3 words calculations. This means that it is not possible to use standard double precision Fortran (16 figures). We get only 9 correct digits with 5 words ($\simeq 35$ figures), therefore no reliable results may be obtained using standard quadruple precision (32 figures). In table I integrals with 70 significant figures are presented.

Once the integrals are calculated, they are used in Ritz variational calculations (see section 4). 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 non positive due to 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 numbers of working words, the integrals were evaluated in a reasonable time in a personal computer. The numerical evaluation of all the integrals used in section IV takes about 81 minutes and the Cholesky decomposition 155 minutes in a 3 GHz. pentium IV 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

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

In order to apply the Ritz variational principle we need to evaluate

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

where

$$\phi_n = C e^{-\alpha(\xi_1 + \xi_2)} (\xi^n_1 \eta^n_1 \xi^n_2 \eta^n_2 + \xi^n_1 \eta^n_1 \xi^n_2 \eta^n_2) r_{12}^m , \quad (32)$$

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

$$Det(H - ES) = 0 . \quad (33)$$

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 functions 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 $R_{eq} = 1.40108$ and for the correspondent ground state energy $E_0(R_{eq}) = -1.1744759302a.u..$ In the table II we show the energy for $R = 1.4$ as we increase the correlation power $m$. The case $m = 0$ is the non correlated 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 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 letter 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 use the new expressions obtained by Falloon for those special functions [18, 19].

The formulae presented have been successfully tested in numerical calculations for the Born-Oppenheimer hydrogen molecule ground-state energy. In order 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 \(\alpha_{jk}^{ol}\) and \(\tilde{\alpha}_{jk}^{ol}\) taken from ref. [18], which are

\[
\alpha_{jk}^{ol} = \frac{1}{(l+k)(l+k+1)} - \alpha_{0l}^{ol} \sum_{i=0}^{j-1} l_i^{ol} \alpha_{j-i-1,k}^{ol} - (a_{0lk} \alpha_{j-1,k+2}^{ol} + \beta_{0lk} \alpha_{j-1,k}^{ol} + \gamma_{0lk} \alpha_{j-1,k-2}^{ol})
\]

(34)

\[
a_{0lk} = \frac{(l+k+1)(l+k+2)}{(2l+2k+3)(2l+2k+5)},
\]

(35)

\[
\beta_{0lk} = \frac{1}{2} \left(1 + \frac{1}{(2l+2k-1)(2l+2k+3)}\right),
\]

(36)

\[
\gamma_{0lk} = \frac{(l+k)(l+k-1)}{(2l+2k-3)(2l+2k-1)},
\]

(37)

\[
l_0^{ol} = l(l+1), \quad l_1^{ol} = \beta_{000}, \quad l_j^{ol} = a_{000} \alpha_{j-1,2}^{ol} + \gamma_{000} \alpha_{j-1,-2}^{ol} \quad j \geq 2.
\]

(38)
\[ \tilde{\alpha}_{jk}^{0l} = \frac{1}{(l+k)(l+k+1)} - \frac{1}{l+1} \sum_{i=0}^{j-1} \tilde{\alpha}_{j-i-1,k}^{0l} - (\tilde{\alpha}_{0l}^{0l} \alpha_{j-1,k+2}^{0l} + \beta_{0lk}^{0l} \tilde{\alpha}_{j-1,k}^{0l} + \gamma_{0lk}^{0l} \tilde{\alpha}_{j-1,k-1}^{0l}) \]

for \( k = k_0 - 2 \).

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

for \( k = k_0 - 4, k_0 - 6, \ldots \), and \( \tilde{\alpha}_{0l}^{0l} = 1 \) for \( l \) even and \( \tilde{\alpha}_{0l}^{0l} = 1/3 \) for \( l \) odd.

References


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<td>5.0217247073759871252844425511008529326667740399757924034765889006508310 $10^8$</td>
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<td>9.0775171286533976397279142053571939917643899700067007432548746653741653 $10^{10}$</td>
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<td>6</td>
<td>5.6573564424462941895866058785091086834579564620229853905788508489761 $10^{11}$</td>
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<td>7</td>
<td>3.65209422280077022706293063568996178374516785863862566056671385551716 $10^{12}$</td>
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<td>8</td>
<td>2.436167086693777336364554225454787171827894374680492294557768473341409 $10^{13}$</td>
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<tr>
<td>9</td>
<td>1.67659769602840474742547821868417610905158756458370106137853955366283 $10^{14}$</td>
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<tr>
<td>10</td>
<td>1.189031234420327023751316354680105625319722659468108699024410004878311 $10^{15}$</td>
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Table 1: integrals $I_{pqrs}^m$ for $\alpha = \beta = 1.2$ and $p = 12$, $q = 12$, $r = 10$, $s = 10$, $m = -1, \ldots, 10$
<table>
<thead>
<tr>
<th>m</th>
<th>$E(R = 1.4)$</th>
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</thead>
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</tr>
</tbody>
</table>

W. Kolos (1994)[4] -1.174475686
H. Nakatsuji (2004)[5] -1.174475703

Table 2: Variational ground-state energy for the hydrogen molecule with maximum values $p = 5$, $q = 5$, $r = 5$, $s = 5$
Figure 1: Number of correct figures against number of working words for the integral $I_{pqrs}^m$ with $\alpha = \beta = 1.2$, $p = 12$, $q = 12$, $r = 10$, $s = 10$, $m = 7$. 