Exponentially correlated Hylleraas-configuration interaction non-relativistic energy of the ^{1}S ground state of the helium atom

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Abstract

A generalization of the Hylleraas-Configuration Interaction method (Hy-CI) first proposed by Wang, et al.[1], the Exponentially Correlated Hylleraas-Configuration Interaction method (E-Hy-CI) in which the single r_{ij} of an Hy-CI wave function is generalized to a form of the generic type $r_{ij}^{\nu_{ij}} e^{-\omega_{ij} r_{ij}}$, is explored. This type of correlation, suggested by Hirshfelder in 1960, has the right behavior both in the vicinity of the r_{ij} cusp as r_{ij} goes to 0 and as r_{ij} goes to infinity; this work explores whether wave functions containing both linear and exponential r_{ij} factors converge more rapidly than either one alone. The method of calculation of the two-electron E-Hy-CI kinetic energy and electron repulsion integrals in a stable and efficient way using recursion relations is discussed, and the relevant formulas are given.

The convergence of the E-Hy-CI wave function expansion is compared with that of the Hy-CI wave function without exponential correlation factors, demonstrating both convergence acceleration and an improvement in the accuracy for the same basis. This makes the application of the E-Hy-CI method to systems with $N > 4$, for which this formalism with at most a single $r_{ij}^{\nu_{ij}} e^{-\omega_{ij} r_{ij}}$ factor per term leads to solvable integrals, very promising. E-Hy-CI method variational calculations with up to 10080 expansion terms are reported for the ground ^1S state of the neutral helium atom, with a resultant nonrelativistic energy of -2.9037 2437 7034 1195 9831 1084 hartree for the best expansion.

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[1]C. Wang, P. Mei, Y. Kurokawa, H. Nakashima, and H. Nakatsuji, *Phys. Rev. A*, **85**, 042512 (2012).

I. Introduction

Variational methods based on explicitly correlated wave functions are known to give the most accurate upper bounds to energy states, and hence the inclusion of terms containing the interelectronic distance r_{ij} in the wave function has become increasingly common, at least for few-electron atomic systems ($N \leq 4$) (so common in fact that a book dealing entirely with explicitly correlated wave functions has been produced [1]; for a recent article see [2]). Wave functions that are commonly referred to now as Hylleraas (Hy) follow the landmark calculation of Hylleraas [3] by employing powers of the interelectronic distance in the wave function. The Hylleraas-Configuration Interaction (Hy-CI) technique (developed by Sims and Hagstrom [4] and also independently by Woźnicki [5]) differs from the traditional Hy development by employing at most a single, linear r_{ij} factor with traditional Configuration Interaction (CI) orbital bases in each Configuration State Function (CSF). While the work of Hylleraas demonstrated that two-electron atoms could be calculated accurately (for that time) with powers of r_{12}, it was Handy [6] who demonstrated that linear terms alone were sufficient for high accuracy for He. Hy-CI in its current incantation utilizes only linear terms in r_{ij}, hence r_{12}/f_{12} [1, 2, 7, 8] methods are related to Hy-CI but outside the scope of this study (but see Ruiz [9] for a discussion of CI-r_{12} and a comparison with Hy-CI in the two-electron He atom case). In an interesting new development, Nakashima and Nakatsuji have introduced Hy-CI into their free-complement chemical formula theory (FC-CFT) [10, 11, 12]. The other common exponentially correlated wave function, the exponentially correlated Gaussian (ECG) [1] wave function, in contrast to Hy and Hy-CI wave functions has the r_{ij} correlation appearing as Gaussian exponentials.

In this paper a generalization of the Hy-CI method first proposed by Wang, Mei, Kurokawa, Nakashima and Nakatsuji [13], the Exponentially correlated Hylleraas-Configuration Interaction (E-Hy-CI) method[2] in which the single r_{ij} of an Hy-CI wave function is generalized to a form of the generic type $r_{ij}^{\nu_{ij}} e^{-\omega_{ij} r_{ij}}$, i.e., an exponentially correlated Slater-type orbital (STO) factor, is explored. Pairing an exponential r_{12} factor with linear r_{12} was first suggested for helium by Hirshfelder in 1960 [14], who suggested that this type of correlation factor has the right behavior in the vicinity of the r_{12} cusp, and also has the

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[2]In their paper Wang et al. [13] refer to this as extended Hy-CI. The authors of this paper prefer exponentially correlated Hy-CI since there is more than one way Hy-CI could be extended and exponentially correlated makes clear that the extension is an exponential r_{ij} factor.

right behavior as r_{12} goes to infinity, but he did no calculations. Whether functions having both linear and exponential r_{ij} factors might be more rapidly convergent than either one alone remained to be seen. Exponentially correlated r_{12} was shown by Thakkar and Smith [15] to give very good results for helium-like ions even with rather compact wave functions[3]. However as pointed out by Harris [17, 18], calculations based on exponentially correlated STOs have been around since then, but they have only become practical (for $N > 2$ electrons) after the publication of an extrodinary paper by Fromm and Hill [19][4]. The E-Hy-CI proposal has been followed by many papers discussing the integrals arising in E-Hy-CI [13, 22, 23, 17, 18], but there have been no atomic or molecular structure E-Hy-CI calculations other than an examination of optimized values of ω_{ij} for the E-Hy-CI wave function by Nakatsuji which is referred to as unpublished in [13]. The present contribution calculates the ground ^{1}S state of helium and compares the result with previous CI, Hy, and Hy-CI calculations [16] of the same state.

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[3]0.01 μhartree energy for He with 66 terms. For comparison, Sims and Hagstrom [9, 16] used 210 terms in their Hy calculation to achieve a comparable result.

[4]As pointed out by Thakkar [20], the use of exponentially correlated wave functions dates back to Slater [21] and Hylleraas [3]. See Harris [17, 18] and references therein for a detailed discussion of the exponential r_{ij} line of development.

II. Variational Calculations

For N_e electrons, the total non-relativistic, stationary-point-nucleus energy E_{NR} is defined as the exact solution (eigenvalue) of the time-independent, non-relativistic Schrödinger equation

$$H_{NR}\Psi(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_{N_e}) = E_{NR}\Psi(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_{N_e}), \tag{1}$$

where the Hamiltonian H_{NR} is defined as (in atomic units)

$$H_{NR} = \sum_{i=1}^{N_e} \mathcal{H}_i + \sum_{i<j}^{N_e} r_{ij}^{-1}. \tag{2}$$

Here $\mathcal{H}_i = \mathcal{T}_i + \mathcal{V}_i$, $\mathcal{H}_i$ being a one electron operator (electron i) consisting of a kinetic energy part $\mathcal{T}_i = -\frac{1}{2}\nabla_i^2$ and a nuclear attraction part $\mathcal{V}_i = -Z/r_i$. N_e denotes the number of electrons and Z the corresponding nuclear charge.

The E-Hy-CI wave function for N_e electron atomic states is

$$\Psi = \sum_{K=1}^{N} C_K \Phi_K, \tag{3}$$

where

$$\Phi_K = \Lambda(r_{ij}^{\nu_K}\mathrm{e}^{-\omega_K r_{ij}} \prod_{s=1}^{N_e}\{\phi_{K_s}(\mathbf{r_s})\}\Theta_K) = O_{as}O_{L,M_L}O_{S,M_S}(r_{ij}^{\nu_K}\mathrm{e}^{-\omega_K r_{ij}} \prod_{s=1}^{N_e}\{\phi_{K_s}(\mathbf{r_s})\}\Theta_K) \tag{4}$$

denotes the Kth antisymmetrized spin and angular momentum projected explicitly correlated Configuration State Function (CSF). O_{L,M_L} and O_{S,M_S} are idempotent orbital and spin angular momentum projection operators of the Löwdin type [24] for a state of total quantum numbers L, M_L, S, M_S (Russell–Saunders (LS) coupling is assumed). Each term K contains at most one explicitly correlated factor $r_{ij}^{\nu_K}\mathrm{e}^{-\omega_K r_{ij}}$ which in addition to the Hy-CI case with $\omega_K = 0$ can also have $\omega_K \neq 0$. In practice it is sufficient to take ν_K equal to

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0 or 1, with $\nu_K = 1$, $\omega_K = 0$ the Hy-CI case and $\nu_K = 0$, $\omega_K = 0$ the CI case. Θ_K is a primitive spin product function for term K and $\phi_{K_s}(\mathbf{r_s})$ represents the sth basis orbital in the Kth term.

The basis orbitals are un-normalized Slater-type orbitals (STOs) $\phi(\mathbf{r})$ which are defined as

$$\phi_i(\mathbf{r}) = [n_i, l_i, m_i]_{\alpha_i} = r^{n_i - 1} e^{-\alpha_i r} Y_{l_i}^{m_i}(\theta, \phi), \tag{5}$$

where $Y_l^m(\theta, \phi)$ is a normalized spherical harmonic in the Condon and Shortley phase convention [25]. With this choice of phase convention, the spherical harmonics satisfy

$$Y_{l_i}^{m_i*}(\theta, \phi) = (-1)^{m_i} Y_{l_i}^{-m_i}(\theta, \phi). \tag{6}$$

O_{as} is the idempotent antisymmetry projection operator.

The coefficients C_K in Equation 3 are found in this work by solving the generalized eigenvalue problem

$$\mathbf{H}\mathbf{C} = E\mathbf{S}\mathbf{C}, \tag{7}$$

$$(\mathbf{H} - E_0\mathbf{S})\mathbf{C} = (E - E_0)\mathbf{S}\mathbf{C}, \tag{8}$$

$$\mathbf{C} = (E - E_0)(\mathbf{H} - E_0\mathbf{S})^{-1}\mathbf{S}\mathbf{C}, \tag{9}$$

where the matrix elements are given by $\mathcal{H}_{KL} = \langle \Phi_K | \mathcal{H} | \Phi_L \rangle$ and $\mathcal{S}_{KL} = \langle \Phi_K | \Phi_L \rangle$ with the Hamiltonian H given by Equation 2 and E_0 is some starting approximation for the eigenvalue E of interest.

(Shifted) inverse iteration [26] is the application of the power method [27] to $\mathbf{A}^{-1} = (\mathbf{H} - E_0\mathbf{S})^{-1}$ in the solution process used for solving for $\mathbf{C}$ in Equation 9 and leads to the iteration formula

$$\mathbf{v}_{k+1} = \mathbf{A}^{-1}\mathbf{S}\mathbf{v}_k, \ k = 0, 1, 2, \dots \tag{10}$$

with a convergence criterion for E, computed from

$$E_k = E_0 + \frac{\mathbf{v}_{k+1} \cdot \mathbf{S}\mathbf{v}_k}{\mathbf{v}_{k+1} \cdot \mathbf{S}\mathbf{v}_{k+1}}, \ k = 0, 1, 2, \dots \tag{11}$$

which converges rapidly to E provided that the trial E_0 is sufficiently close to the desired eigenvalue, which turned out to be 5 digit accuracy in these calculations. In addition to a suitable E_0, shifted inverse iteration requires a starting vector $\mathbf{v}_0$ (which was usually taken to be a vector of all 1s) and an efficient factorization for $\mathbf{A}^{-1}$ in Equation 10, which for us is

$$\mathbf{A}^{-1} = \mathbf{L}^T\mathbf{D}^{-1}\mathbf{L}, \tag{12}$$

where $\mathbf{D}$ is a diagonal matrix and $\mathbf{L}$ is the implicit representation of the lower triangular matrix $\mathbf{L}$ in terms of Gaussian transformations [28]. Except for some of the shorter expansions reported in Tables II and III, all results reported in this article were obtained using real*32 extended precision (quad-double-with exponent or QDE, 256-bit, ≈ 64 digits) floating point arithmetic, and the Message Passing Interface (MPI) Standard [29] was used to parallelize the code.

III. Method of Calculation

For two electrons, following Hy-CI [16] spin can be eliminated and the E-Hy-CI wave function becomes:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{K=1}^{N} C_K \Phi_K(\mathbf{r}_1, \mathbf{r}_2), \tag{13}$$

where the terms Φ_K are specifically of the form

$$\Phi_K(\mathbf{r}_1, \mathbf{r}_2) = r_{12}^{\nu_K} e^{-\omega_K r_{12}} (1 \pm P_{12}) O_{L,M_L}(\phi_{K_1}(\mathbf{r}_1)\phi_{K_2}(\mathbf{r}_2)). \tag{14}$$

P_{12} is the operator which permutes electrons 1 and 2, and the plus sign is for singlet levels, the minus sign for triplet levels. Equation 2 becomes

$$H_{NR} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{12}, \tag{15}$$

where $\mathcal{H}_{12} = r_{12}^{-1}$.

In the generalized eigenvalue problem $\mathbf{HC} = \lambda\mathbf{SC}$, matrix element H_{KL} is

$$H_{KL} = \langle \Phi_K | \mathcal{H} | \Phi_L \rangle = \langle \Lambda \Phi_K^P | \mathcal{H} | \Lambda \Phi_L^P \rangle, \tag{16}$$

where Φ_K^P denotes the Kth primitive (unprojected) function as given above. S_{KL} is similar, with $\mathcal{H}$ replaced by the unit operator 1.

The projection reduction of these matrix elements is same projection reduction used in lithium [30] and in beryllium [31] and is discussed in Appendix A of those references. The helium case is simpler so just the result is given here, which is that H_{KL} is given by

$$H_{KL} = \langle g_K f_K | \mathcal{H} | O_{L,M_L} B(g_L f_L) \rangle. \tag{17}$$

In Equation 17 one can apply O_{L,M_L} either before or after applying $B = 1 + P_{12}$. Here the permutations B are applied to $g_L f_L$ first, then the O_{L,M_L} projection is done on the resultant. The O_{L,M_L} projection is applied only on the orbital products since $g_L = r_{ij}^{\nu_L}$ commutes with O_{L,M_L} [4].

Now to generalize Hy-CI to E-Hy-CI for the two electron He case, one merely has to take the correlation factor g_K to be $g_K = r_{ij}^{\nu_K} e^{-\omega_K r_{12}}$ in the formulas above since $e^{-\omega_K r_{12}}$ has the same symmetry properties as r_{12}. Thus H_{KL} becomes

$$H_{KL} = \langle \phi_{K1}(\mathbf{r}_1)\phi_{K2}(\mathbf{r}_2) r_{12}^{\nu_K} e^{-\omega_K r_{12}} | \mathcal{H} | r_{12}^{\nu_L} e^{-\omega_L r_{12}} (1 + P_{12}) \phi_{L1}(\mathbf{r}_1)\phi_{L2}(\mathbf{r}_2) \rangle. \tag{18}$$

A. Electron Repulsion and Overlap Integrals

With this wave function, the most general exponentially correlated integrals that have to be evaluated are of the form

$$I_{\mathcal{R}} = \langle \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) r_{12}^{\nu} \mathrm{e}^{-\omega r_{12}} | \mathcal{R} | r_{12}^{\nu'} \mathrm{e}^{-\omega' r_{12}} \phi_1'(\mathbf{r}_1)\phi_2'(\mathbf{r}_2) \rangle, \tag{19}$$

where the operator $\mathcal{R} = 1$ for overlap integrals and $\mathcal{R} = \mathcal{H}_{12} = r_{12}^{-1}$ for electron repulsion integrals. Hence the integral

$$I = \int r_{12}^{\nu_{12}} \mathrm{e}^{-\omega_{12} r_{12}} \Omega_1(\mathbf{r}_1)\Omega_2(\mathbf{r}_2) \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \tag{20}$$

is the integral to be evaluated here, with $\omega_{12} = \omega + \omega'$, $\nu_{12} = \nu + \nu'$ the overlap integral, $\nu_{12} = \nu + \nu' - 1$ the electron repulsion integral, and $\nu_{12} \geq -1$. The Ωs are "charge distributions" made up of products of the STOs, i.e.,

$$\Omega(\mathbf{r}) = \phi^*(\mathbf{r})\phi'(\mathbf{r}) = [n, l, m]_{\alpha}^* [n', l', m']_{\alpha'}. \tag{21}$$

The charge distributions $\Omega_i(\mathbf{r})$ can be expanded in terms of STO-like functions $f_i(\mathbf{r})$

$$f_i(\mathbf{r}) = [N_i, L_i, M_i]_{\omega_i} = r^{N_i-1} \mathrm{e}^{-\omega_i r_i} Y_{L_i}^{M_i}(\theta, \varphi); \tag{22}$$

the formula is [32]

$$\Omega_i(\mathbf{r}) = \sum_{L_i} \left\{ \frac{(2L_i+1)}{4\pi} \right\}^{1/2} c^{L_i}\left(l_i', m_i'; l_i, m_i\right) f_i(\mathbf{r}), \tag{23}$$

where $N_i = n_i + n_i' - 1$ and the exponents are $w_i = \alpha_i + \alpha_i'$. The L_i satisfy the triangular inequality $|l_i - l_i'| \leq L_i \leq l_i + l_i'$, with $l_i + l_i' + L_i = 2g$ (g integral, i.e., the summation goes in steps of 2), and with the further restriction $L_i \geq |M_i|$, $M_i = m_i' - m_i$. The c^{L_i} are standard Condon and Shortley coefficients (the so-called c^ks) [32, 33, 25, 34].

Using Equations 6 and 23, I becomes

$$I = \sum_{L_1, L_2} \prod_{i=1}^{2} \left\{ \left(\frac{(2L_i+1)}{4\pi} \right)^{\frac{1}{2}} (-1)^{M_1} c^{L_i}(l_i', m_i'; l_i, m_i) \right\} J(L_1, L_2), \tag{24}$$

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where the factor $J(L_1, L_2)$ is

$$J(L_1, L_2) = \int r_{12}^{\nu_{12}} e^{-\omega_{12}r_{12}} r_1^{N_1-1} r_2^{N_2-1} e^{-\omega_1 r_1 - \omega_2 r_2} Y_{L_1}^{-M_1*}(1) Y_{L_2}^{M_2}(2) d\mathbf{r}_1 d\mathbf{r}_2. \quad (25)$$

$J(L_1, L_2)$ is a straightforward generalization to E-Hy-CI of the Hy-CI radial integral J_1 introduced by Sims and Hagstrom in 1971 [32][5].

In Hy-CI [32], with $f(r_{12}) = r_{12}^p$, the Legendre expansion for r_{ij}^p with p odd

$$r_{ij}^p = \sum_{n=0}^{\infty} B_n(r_{ij}, p) P_n(cos\theta_{ij}), \quad (26)$$

has been used by the present authors to facilitate integration of $J(L_1, L_2)$ over the polar coordinates of electrons 1 and 2. An alternate method, first used by Calais and Löwdin [35], has been used by other authors in treating Hy-CI integrals [36, 37, 22, 23]. The method reduces matrix elements like $J(L_1, L_2)$ to radial integrals over the r_1, r_2, r_{12} Hylleraas coordinates by a coordinate system rotation[6]. The same transformation to Hylleraas coordinates[7] transforms $J(L_1, L_2)$ into

$$J(L_1, L_2) = 2\pi \, \delta_{L_1, L_2} \, \delta_{M_1+M_2, 0} \quad (27)$$
$$\times \int_0^{\infty} r_1^{N_1} e^{-\omega_1 r_1} dr_1 \int_0^{\infty} r_2^{N_2} e^{-\omega_2 r_2} dr_2 \int_{|r_1-r_2|}^{r_1+r_2} r_{12}^{\nu_{12}+1} e^{-\omega_{12}r_{12}} P_L(cos\theta_{12}) dr_{12}$$
$$= 4\pi \, \delta_{L_1, L_2} \, \delta_{M_1+M_2, 0} \, I_L(N_1, N_2; \omega_1, \omega_2, \omega_{12}; \nu_{12}),$$

where

$$I_L(N_1, N_2; \omega_1, \omega_2, \omega_{12}; \nu_{12}) = \frac{1}{2}$$
$$\times \int_0^{\infty} r_1^{N_1} e^{-\omega_1 r_1} dr_1 \int_0^{\infty} r_2^{N_2} e^{-\omega_2 r_2} dr_2 \int_{|r_1-r_2|}^{r_1+r_2} r_{12}^{\nu_{12}+1} e^{-\omega_{12}r_{12}} P_L(cos\theta_{12}) dr_{12}, \quad (28)$$

the two electron E-Hy-CI analog of Eq. (A.16) [39], is the integral evaluated by Wang et al.[8]. L[9] is the value of $L_1 = L_2$ when $J(L_1, L_2) \neq 0$. Note that these are purely radial

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[5]See Eq. 29 in [32].

[6]See Drake [38] for an Hy method exposition for two-electron states of arbitrary angular momentum, and [39] for the Hy-CI case.

[7]See Sec. III in Calais and Löwdin [35] for details. Equation 27 agrees with Calais and Löwdin's Equation 17.

[8]Equation 20 in [13].

[9]L is being used here to refer to charge distributions (See Equation 22) and is not to be confused with the L quantum number of the atom in LS coupling, which for S states is 0.

integrals, dependent solely on r_1, r_2, and r_{12}, because

$$cos\theta_{12} = \frac{r_1^2 + r_2^2 - r_{12}^2}{2r_1 r_2} \tag{29}$$

and the substitution has to occur before the integration.

Substituting Equation 27 into Equation 24, we obtain

$$I = (-1)^{M_1} \delta_{M_1+M_2,0} \tag{30}$$
$$\times \sum_L (2L+1) c^L(l_1', m_1'; l_1, m_1) c^L(l_2', m_2'; l_2, m_2) I_L(N_1, N_2; \omega_1, \omega_2, \omega_{12}; \nu_{12}),$$

where L needs to satisfy all of the following conditions:

1. $|l_1' - l_1| \le L \le l_1' + l_1$, $l_1' + l_1 + L = 2g$ (g integral)

2. $|l_2' - l_2| \le L \le l_2' + l_2$, $l_2' + l_2 + L = 2g'$ (g' integral)

3. $L \ge |M_1|$, $M_1 = -M_2$,

and the range of L from the first condition must overlap the range of L from the second condition. For most L_1, L_2 cases arising in practice, the range of L will be quite limited.

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B. Kinetic Energy and Nuclear Attraction Integrals

With this wave function, exponentially correlated kinetic energy integrals that have to be evaluated are of the form

$$I_{\mathcal{T}_i} = \langle \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) r_{12}^\nu e^{-\omega r_{12}} | \mathcal{T}_i | r_{12}^{\nu'} e^{-\omega' r_{12}} \phi_1'(\mathbf{r}_1)\phi_2'(\mathbf{r}_2) \rangle. \tag{31}$$

For two electrons, the simplest way to do the Hy-CI case has been known for years, which is to use a transformation known as the Kolos-Roothaan transformation after the paper in which Kolos and Roothaan used it in a pioneering calculation on the hydrogen molecule [40]. In a companion article in the same journal, Roothaan and Weiss use this transformation in a calculation on the helium atom [41] and say that the transformation was shown to them by Kolos. The transformation has been proved by both Ruiz and Padhy for Hy-CI[10] and an analogous transformation has been proved by Padhy for E-Hy-CI[11] to show that, when $\mathcal{T}_i = \mathcal{T}_1$,[12]

$$
\begin{aligned}
I_{\mathcal{T}_1}^{\nu,\nu'=0} &= \langle \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) e^{-\omega r_{12}} | \mathcal{T}_1 | e^{-\omega' r_{12}} \phi_1'(\mathbf{r}_1)\phi_2'(\mathbf{r}_2) \rangle \tag{32} \\
\\
&= \frac{1}{2} \int d\mathbf{r}_2 \phi_2^*(\mathbf{r}_2)\phi_2'(\mathbf{r}_2) \int d\mathbf{r}_1 e^{-(\omega+\omega')r_{12}} \\
&\quad \times \left[\omega\omega' \phi_1^*(\mathbf{r}_1)\phi_1'(\mathbf{r}_1) - \left(\frac{\omega' \phi_1'(\mathbf{r}_1) \nabla_1^2 \phi_1^*(\mathbf{r}_1) + \omega \phi_1^*(\mathbf{r}_1) \nabla_1^2 \phi_1'(\mathbf{r}_1)}{\omega + \omega'} \right) \right].
\end{aligned}
$$

$I_{\mathcal{T}_1}^{\nu,\nu'=0}$ is now in a form in which ∇_1^2 is just a one-electron operation which can be written as

$$\nabla_1^2 = \frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial}{\partial r_1} - \frac{\mathbf{l}_1^2}{r_1^2}, \tag{33}$$

where $\mathbf{l}^2$ is the squared resultant one-electron orbital angular momentum operator $\mathbf{l}^2 = l_x^2 + l_y^2 + l_z^2$ which, when operating on a $\phi_i(\mathbf{r}_i)$, has the property that

$$\mathbf{l}_i^2 \phi_i(\mathbf{r}_i) = l_i(l_i+1)\phi_i(\mathbf{r}_i). \tag{34}$$

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[10]Ruiz in Appendix B in [39] and Padhy in Appendix C in [23].
[11]Padhy in Appendix D in [23].
[12]This relationship is used in [22].

This gives for $\mathcal{T}_1\phi_1(\mathbf{r}_1)$

$$\mathcal{T}_1\phi_1(\mathbf{r}_1) = -\frac{1}{2}\nabla_1^2\phi_1(\mathbf{r}_1) = \left[\frac{(l_1+n_1)(l_1-n_1+1)}{2r_1^2} + \frac{n_1\alpha_1}{r_1} - \frac{\alpha_1^2}{2}\right]\phi_1(\mathbf{r}_1) \qquad (35)$$

so that, since $\mathcal{H}_1 = \mathcal{T}_1 + \mathcal{V}_1 = \mathcal{T}_1 - Z/r_1$,

$$
\begin{aligned}
I_{\mathcal{H}_1}^{\nu,\nu'=0} &= \langle\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)e^{-\omega r_{12}}|\mathcal{T}_1 - \frac{Z}{r_1}|e^{-\omega' r_{12}}\phi_1'(\mathbf{r}_1)\phi_2'(\mathbf{r}_2)\rangle \qquad (36)\\
&= \frac{1}{2}\left[\omega\omega' - \frac{(\omega'\alpha_1^2+\omega\alpha_1'^2)}{\omega+\omega'}\right]\langle\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)e^{-\omega r_{12}}|1|e^{-\omega' r_{12}}\phi_1'(\mathbf{r}_1)\phi_2'(\mathbf{r}_2)\rangle\\
&+ \frac{1}{2}\left[\frac{\omega'(l_1+n_1)(l_1-n_1+1)+\omega(l_1'+n_1')(l_1'-n_1'+1)}{\omega+\omega'}\right]\\
&\qquad \times\langle\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)e^{-\omega r_{12}}|\frac{1}{r_1^2}|e^{-\omega' r_{12}}\phi_1'(\mathbf{r}_1)\phi_2'(\mathbf{r}_2)\rangle\\
&+ \left[\frac{\omega'n_1\alpha_1+\omega n_1'\alpha'_1}{\omega+\omega'} - Z\right]\langle\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)e^{-\omega r_{12}}|\frac{1}{r_1}|e^{-\omega' r_{12}}\phi_1'(\mathbf{r}_1)\phi_2'(\mathbf{r}_2)\rangle,
\end{aligned}
$$

where the nuclear attraction term has been added (with the appropriate sign) to the r_1^{-1} component.

$I_{\mathcal{H}_1}^{\nu,\nu'\neq 0}$ can be obtained from $I_{\mathcal{H}_1}^{\nu,\nu'=0}$ by parametric differentiation of $I_{\mathcal{H}_1}^{\nu,\nu'=0}$ with respect to ω and/or ω' as required [22].

The result for $I_{\mathcal{H}_1}^{\nu,\nu'}$, which is the general expression valid for $\nu,\nu' = \{0,0;0,1;1,0;1,1\}$,

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is

$$
\begin{aligned}
I_{\mathcal{H}_1}^{\nu,\nu'} &= \frac{1}{2}\left[\omega\omega' - \frac{(\omega'\alpha_1^2 + \omega\alpha_1'^2)}{\omega_{12}}\right]\ \langle\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)e^{-\omega r_{12}}|r_{12}^{\nu_{12}}|e^{-\omega' r_{12}}\phi_1'(\mathbf{r}_1)\phi_2'(\mathbf{r}_2)\rangle \quad (37)\\
&+ \frac{1}{2}\left[\frac{\omega'(l_1+n_1)(l_1-n_1+1) + \omega(l_1'+n_1')(l_1'-n_1'+1)}{\omega_{12}}\right]\\
&\qquad \times \langle\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)e^{-\omega r_{12}}|\frac{r_{12}^{\nu_{12}}}{r_1^2}|e^{-\omega' r_{12}}\phi_1'(\mathbf{r}_1)\phi_2'(\mathbf{r}_2)\rangle\\
&+ \left[\frac{(\omega'n_1\alpha_1 + \omega n_1'\alpha'_1)}{\omega_{12}} - Z\right]\ \langle\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)e^{-\omega r_{12}}|\frac{r_{12}^{\nu_{12}}}{r_1}|e^{-\omega' r_{12}}\phi_1'(\mathbf{r}_1)\phi_2'(\mathbf{r}_2)\rangle\\
&+ \frac{(\omega'\nu - \omega\nu')}{\omega_{12}^2}(n_1\alpha_1 - n_1'\alpha_1')\ \langle\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)e^{-\omega r_{12}}|\frac{r_{12}^{\nu_{12}-1}}{r_1}|e^{-\omega' r_{12}}\phi_1'(\mathbf{r}_1)\phi_2'(\mathbf{r}_2)\rangle\\
&+ \frac{1}{2}\frac{(\omega'\nu - \omega\nu')}{\omega_{12}^2}\left[(l_1+n_1)(l_1-n_1+1) - (l_1'+n_1')(l_1'-n_1'+1)\right]\\
&\qquad \times \langle\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)e^{-\omega r_{12}}|\frac{r_{12}^{\nu_{12}-1}}{r_1^2}|e^{-\omega' r_{12}}\phi_1'(\mathbf{r}_1)\phi_2'(\mathbf{r}_2)\rangle\\
&+ \frac{1}{2}\left[-(\omega\nu' + \omega'\nu) + \frac{(\omega'\nu - \omega\nu')(\alpha_1'^2 - \alpha_1^2)}{\omega_{12}^2}\right]\\
&\qquad \times \langle\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)e^{-\omega r_{12}}|r_{12}^{\nu_{12}-1}|e^{-\omega' r_{12}}\phi_1'(\mathbf{r}_1)\phi_2'(\mathbf{r}_2)\rangle\\
&+ \frac{1}{2}\nu\nu'\left[1 + \frac{(\omega'-\omega)(\alpha_1'^2 - \alpha_1^2)}{\omega_{12}^3}\right]\ \langle\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)e^{-\omega r_{12}}|1|e^{-\omega' r_{12}}\phi_1'(\mathbf{r}_1)\phi_2'(\mathbf{r}_2)\rangle\\
&+ \frac{1}{2}\nu\nu'\frac{(\omega'-\omega)}{\omega_{12}^3}\left[(l_1+n_1)(l_1-n_1+1) - (l_1'+n_1')(l_1'-n_1'+1)\right]\\
&\qquad \times \langle\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)e^{-\omega r_{12}}|\frac{1}{r_1^2}|e^{-\omega' r_{12}}\phi_1'(\mathbf{r}_1)\phi_2'(\mathbf{r}_2)\rangle\\
&+ \nu\nu'\left[\frac{(\omega'-\omega)}{\omega_{12}^3}(n_1\alpha_1 - n_1'\alpha_1')\right]\ \langle\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)e^{-\omega r_{12}}|\frac{1}{r_1}|e^{-\omega' r_{12}}\phi_1'(\mathbf{r}_1)\phi_2'(\mathbf{r}_2)\rangle
\end{aligned}
$$

where $\omega + \omega'$ has been replaced with ω_{12} and $\nu + \nu'$ with ν_{12} where appropriate. It agrees with the E-Hy-CI kinetic energy formulas derived in [22] when a typo in Equation 25 (the coefficient of $\langle S/r_1^2\rangle$ should have ω in the numerator rather than ω') is corrected. Equation 37 is expressed in terms of integrals which have the same structure as Equation 19 with the operator $R = \frac{r_{12}^{N_{12}}}{r_1^s r_2^t}$, so Equation 30 holds with the caveats that $\nu_{12} = N_{12} = \{0, 1, 2\}$, $N_1 = n_1 + n_1' - 1 - s$, $N_2 = n_2 + n_2' - 1 - t$, and $s, t = \{0, 1, 2\}$.

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C. Calculation of the Radial Integrals

As pointed out in the development leading up to Equation 30, a closed form expression for the radial integrals to be evaluated,

$$
I_L(N_1, N_2; \omega_1, \omega_2, \omega_{12}; \nu_{12}) = \frac{1}{2}
$$
$$
\times \int_0^\infty r_1^{N_1} e^{-\omega_1 r_1} dr_1 \int_0^\infty r_2^{N_2} e^{-\omega_2 r_2} dr_2 \int_{|r_1-r_2|}^{r_1+r_2} r_{12}^{\nu_{12}+1} e^{-\omega_{12} r_{12}} P_L(\cos\theta_{12}) dr_{12},
\tag{38}
$$

has been given by Wang et al.[13]. It will prove useful to consider the case of all s STOs, where for all of the s STOs $l_i = 0$. Eq. 20 of [13] reduces to

$$
I_0(N_1, N_2; \omega_1, \omega_2, \omega_{12}; \nu_{12}) = \frac{1}{2} \frac{(\nu_{12}+1)!}{\omega_{12}^{\nu_{12}+2}} \sum_{i=0}^{\nu_{12}+1} \frac{\omega_{12}^i}{i!}
$$
$$
\times \left\{ \sum_{j=0}^{i} \binom{i}{j} [(-1)^j A(N_2+j, \omega_2-\omega_{12}) - A(N_2+j, \omega_2+\omega_{12})] A(N_1+i-j, \omega_1+\omega_{12}) \right.
\tag{39}
$$
$$
\left. - \sum_{j=0}^{N_2} \binom{N_2}{j} [(-1)^i A(i+j, \omega_2-\omega_{12}) - A(i+j, \omega_2+\omega_{12})] A(N_1+N_2-j, \omega_1+\omega_2) \right\},
$$

where

$$
A(n, \alpha) = \int_0^\infty r^n e^{-\alpha r} dr
\tag{40}
$$

and $\nu_{12} = \{-1, ..., 2\}$, $N_1 = n_1 + n_1' - 1 - s$, $N_2 = n_2 + n_2' - 1 - t$ with $s, t = \{0, 1, 2\}$. Clearly $n \geq 0$ in $A(n, \alpha)$ except for the kinetic energy case with s or $t = 2$ because $j \leq i$ and the n quantum number for s STOs is ≥ 1 which makes $N_1 \geq 1 - s$ and $N_2 \geq 1 - t$. Furthermore it is only N_1 or N_2 which can be nonnegative (but not both at the same time), and the presence of ω_{12} in the denominator of Equation 39 means, as pointed out by Wang, et al. [13], that this formula is not suitable for numerical evaluation when $\omega_{12} = 0$ (the Hy-CI case). Furthermore the divergent case of n < 0 in $A(n, \alpha)$ is one which does occur and formulas with alternating signs can introduce stability problems. For all of these reasons

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[13]Equation 20 in Wang, et al. [13].

Equation 20 in Wang, et al. [13] is not suitable for high precisioon He atom energy calcula-tions. Instead $P_0(cos\theta_{12}) = 1$ is used to relate $I_0(N_1, N_2; \omega_1, \omega_2, \omega_{12}; \nu_{12})$ to the consider-able body of work that has been done on these integrals by researchers using exponentially correlated wave functions. This is accomplished by relating $I_0(N_1, N_2; \omega_1, \omega_2, \omega_{12}; \nu_{12})$ to the generic radial integral $\Gamma_{l,m,n}(\alpha, \beta, \gamma)$ of Harris [42, 43], that is

$$I_0(N_1, N_2; \omega_1, \omega_2, \omega_{12}; \nu_{12}) = \Gamma_{N_1, N_2, \nu_{12}+1}(\omega_1, \omega_2, \omega_{12}), \tag{41}$$

where

$$\Gamma_{l,m,n}(\alpha, \beta, \gamma) = \tfrac{1}{2} \int_0^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1-r_2|}^{r_1+r_2} dr_{12} r_1^l r_2^m r_{12}^n e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}}. \tag{42}$$

Note that with this definition of Γ, the I_0 radial integral and Γ are identical.

This definition of Γ is not the same as the one used by Harris's research group in an earlier publication [44], which is the definition used by Korobov [45], and later, Wang, et al. [13][14]. The difference can best be seen by starting from the way Harris relates it to the integral over the full three-dimensional space of $d\mathbf{r}_1$ and $d\mathbf{r}_2$. In his later papers [42, 43] this is

$$\Gamma_{l,m,n}(\alpha, \beta, \gamma) = \tfrac{1}{16\pi^2} \int_0^\infty d\mathbf{r}_1 \int_0^\infty d\mathbf{r}_2 r_1^{l-1} r_2^{m-1} r_{12}^{n-1} e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}}. \tag{43}$$

The transformation to radial integrals over the r_1, r_2, r_{12} Hylleraas coordinates[15] trans-forms Equation 43 into Equation 42.

In contrast, in the earlier publication [44] (the one followed by Wang, et al.), $\Gamma_{l,m,n}(\alpha, \beta, \gamma)$ is given by

$$\Gamma_{l,m,n}(\alpha, \beta, \gamma) = \tfrac{1}{8\pi^2} \int_0^\infty d\mathbf{r}_1 \int_0^\infty d\mathbf{r}_2 r_1^{l-1} r_2^{m-1} r_{12}^{n-1}. \tag{44}$$

With this earlier relation, the same transformation to radial integrals over the r_1, r_2, r_{12} Hylleraas coordinates leads to

$$\Gamma_{l,m,n}(\alpha, \beta, \gamma) = \int_0^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1-r_2|}^{r_1+r_2} dr_{12} r_1^l r_2^m r_{12}^n e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}}, \tag{45}$$

which illustrates the factor of 2 difference between the two definitions of Γ (compare Equation 45 to Equation 42). The reason for following Harris's later definition is that

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[14]Equation 39 in Wang, et al. [13].

[15]See Drake [38] for an Hy method exposition for two-electron states of arbitrary angular momentum, and [39] for the Hy-CI case.

his later papers describe an alternate method for treating these integrals with more rapid convergence than the earlier method; the method with the faster convergence (that of Sack, Roothaan, and Kolos [46]) is chosen in this work. This choice has the added bonus that, as mentioned above, the I_0 radial integral and Γ are identical.

The permutational invariance of Equation 43 implies that $\Gamma_{l,-1,n}(\alpha, \beta, \gamma) = \Gamma_{-1,l,n}(\beta, \alpha, \gamma)$, so the evaluation of all $I_0(N_1, N_2; \omega_1, \omega_2, \omega_{12}; \nu_{12})$ breaks down to the evaluation of two separate cases, (1) $\Gamma_{N_1,N_2,\nu_{12}+1}(\omega_1, \omega_2, \omega_{12})$, N_1, N_2, and $\nu_{12} + 1$ nonnegative, and (2) $\Gamma_{-1,N_2,\nu_{12}+1}(\omega_1, \omega_2, \omega_{12})$ with N_2 and $\nu_{12} + 1$ nonnegative. The first case (all indices nonnegative) can be treated by a procedure introduced by Sack, Roothaan, and Kolos [47], which leads to the recurrence formulas [42, 43]

$$\Gamma_{lmn} = \frac{1}{\alpha + \beta} \left[l\Gamma_{l-1,m,n} + m\Gamma_{l,m-1,n} + B_{lmn} \right], \tag{46}$$

$$B_{lmn} = \frac{1}{\alpha + \gamma} \left[lB_{l-1,m,n} + nB_{l,m,n-1} + A_{lmn} \right], \tag{47}$$

$$A_{lmn} = \delta_{l,0} \frac{(m + n)!}{(\beta + \gamma)^{m+n+1}}, \tag{48}$$

where $\Gamma_{l,m,n}(\alpha, \beta, \gamma)$ has been abbreviated as $\Gamma_{l,m,n}$ and B_{lmn} and A_{lmn} are analogous abbreviations. With the definition of Γ given by Equation 42, the starting value for the recursion is found by direct integration [35] to have the value[16]

$$\Gamma_{000} = \frac{1}{(\alpha + \beta)(\alpha + \gamma)(\beta + \gamma)}. \tag{49}$$

The remaining task is to develop a recursion relation and procedures for evaluating $I_L(N_1, N_2, ; \omega_1, \omega_2, \omega_{12}; \nu_{12})$, $L \neq 0$. To accomplish that, the procedures developed by Drake [38] and Yan and Drake [48] were adapted to this case of exponentially correlated STOs. Bonnet's recursion relation for Legendre polynomials

$$(L + 1)P_{L+1}(x) = (2L + 1)xP_L(x) - LP_{L-1}(x) \tag{50}$$

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[16]Starting from Equation 45, Γ_{000} would have 2 in the numerator and Equation 48 would also be multiplied by a factor of 2.

is used in both Equation 38 and Equation 29 to obtain

$$(L+1)\,I_{L+1}(N_1, N_2, \nu_{12}) = \frac{(2L+1)}{2} \times$$
$$\{I_L(N_1+1, N_2-1, \nu_{12}) + I_L(N_1-1, N_2+1, \nu_{12}) - I_L(N_1-1, N_2-1, \nu_{12}+2)\} \tag{51}$$
$$- L\,I_{L-1}(N_1, N_2, \nu_{12}),$$

where the abbreviation $I_L(N_1, N_2, \nu_{12})$ for $I_L(N_1, N_2; \omega_1, \omega_2, \omega_{12}; \nu_{12})$ has been used for clarity. Equation 51 agrees with Efros [49].

$I_1(N_1, N_2, \nu_{12})$ is needed in addition to $I_0(N_1, N_2, \nu_{12})$ to start the recursion. Again using Equation 29, $I_1(N_1, N_2, \nu_{12})$ can be written as

$$I_1(N_1, N_2, \nu_{12}) = \frac{1}{2}\Big\{I_0(N_1+1, N_2-1, \nu_{12}) + I_0(N_1-1, N_2+1, \nu_{12})$$
$$- I_0(N_1-1, N_2-1, \nu_{12}+2)\Big\}. \tag{52}$$

Given a table of $I_0(l, m, n)$ for a sufficiently large range of the parameters l, m, n, which turns out to be l, m, n ranging from $N_i - L$ to $N_i + L$ (from recurring L times) for $N_i = \{N_1, N_2\}$ and $\nu_{12} + 1 \rightarrow \nu_{12} + 1 + 2 \times L$ for ν_{12}, the general radial integral $I_L(N_1, N_2, \nu_{12})$ can now be calculated. Note that in computing the $I_0(l, m, n)$ when l is negative, $I_0(-1, 0, 0)$ is still the starting point for the recursion because this corresponds to the minimum that N_1 or N_2 can be. To show that, remembering the permutational invariance of Equation 43 and that only one of N_1, N_2 can be negative, it is sufficient to consider

$$\min(N_1 = n_1 + n_1' - 1 - s = n_1 + n_1' - 3 = l_1 + l_1' - 1) \tag{53}$$

since for orbital quantum numbers $n \geq l + 1$. But $L = \min(l_1 + l_1', l_2 + l_2')$ implies that $L \leq l_1 + l_1'$, so $N_1 - L \geq N_1 - l_1 - l_1' \geq -1$. When cases other than the two cases treated here arise, as for example in calculations of relativistic and quantum electrodynamic effects, singular integrals can arise. See for example Harris, et al. [44] for how to handle these cases[17]. While this recursion is potentially unstable due to the negative signs in the recursion, the conditions on L lead to a severely limited range of L which restricts the places where differencing errors can occur to the well studied $l < 0$ case [42, 17] and this recursion which appears to be the same as the Efros [49] recursion used effectively for He by Korobov [50].

The recurrence formulas given above in Equation 46 - 48 are treated in detail in Harris [42] and summarized in the Appendix: Boundary Integrals of Harris [17]. The terms on

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[17]Taking into consideration the different definition of Γ in [44] from the one we use here.

the right side of all of these recurrence relations are positive so it is computationally stable (and fast) to evaluate the array A first, then B, evaluating $B_{0,0,n}$ for all n first, then Γ, evaluating $\Gamma(0,0,n)$ for all n first. Case (2), where $l = -1$, is more complicated. Again a starting formula can be found by direct integration, which is (using our definition of Γ)[18]

$$\Gamma_{-1,0,0}(\alpha, \beta, \gamma) = \frac{\{ln(\alpha + \beta) - ln(\alpha + \gamma)\}}{\beta^2 - \gamma^2}. \tag{54}$$

As pointed out by Harris, the optimum procedure depends on $\beta - \gamma$.[19] This case, and what to do when $\beta - \gamma$ is small, is treated in detail in [42] and in the Appendix: Boundary Integrals of Harris [17]. The authors summarize it in the Appendix.

Given that

$$I_L(N_1, N_2, \nu_{12}) = \frac{1}{2} \int_0^\infty r_1^{N_1} e^{-\omega_1 r_1} dr_1 \int_0^\infty r_2^{N_2} e^{-\omega_2 r_2} dr_2 \int_{|r_1 - r_2|}^{r_1 + r_2} r_{12}^{\nu_{12}+1} e^{-\omega_{12} r_{12}} P_L(\cos\theta_{12}) dr_{12} \tag{55}$$

and

$$\Gamma_{l,m,n}(\alpha, \beta, \gamma) = \frac{1}{2} \int_0^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1 - r_2|}^{r_1 + r_2} dr_{12} r_1^l r_2^m r_{12}^n e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}}, \tag{56}$$

we can express I_L in terms of $\Gamma_{l,m,n}(\omega_1, \omega_2, \omega_{12})$. The formula is

$$I_L(N_1, N_2, \nu_{12}) = 2 \sum_{k=0}^{[L/2]} \sum_{q=0}^{L-2k} \sum_{p=0}^{L-2k-q} \frac{(-1)^{k+q}}{2^{2L-2k+1}} \binom{L}{k} \binom{2L-2k}{L} \binom{L-2k}{q} \binom{L-2k-q}{p} \tag{57}$$
$$\times \Gamma_{N_1+L-2k-2q-2p, N_2-L+2k+2p, \nu_{12}+2q+1}(\omega_1, \omega_2, \omega_{12}).$$

This result is twice the result of Wang, et al. (Equation 38 in [13]) due to the differing definitions of $\Gamma_{l,m,n}$, and gives us three different methods for evaluating the radial integrals, namely,

- use Equation 20 in Wang, et al. [13],

- evaluate $\Gamma_{l,m,n}$ using the recurrence formulas Equation 46 - Equation 48 for positive l, m, n and as explained in the Appendix for $\Gamma_{-1,m,n}$. This gives I_0. Use use the recursion formula Equation 51 to recur to higher L values, and

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[18]With the Equation 45 definition, Equation 54 would again be multiplied by a factor of 2.

[19]$\beta - \gamma$ appears in the recursion relations developed for this case, see the Appendix.

- use Equation 57 which expresses I_L in terms of $\Gamma_{l,m,n}$ which is evaluated the same way as in the previous method.

As a check on the formulas (and coding) of I_L, all of the two-electron integrals of Wang et al.[20] were computed using all three methods discussed above[21]. The results agree to the accuracy of their 'correct results', which are the boldface letters in their tables. This includes $L \neq 0$. There are no stability issues in computing Hy-CI integrals for He, since there are no formulas involving alternating signs. The stability issues arising when using STO exponentially correlated wave functions have been discussed by King [51], who points out in Section 7 of that reference the stability issues in formulas involving terms with opposite signs which can lead to serious loss of significant digits when numerical evaluation of the formulas is carried out. We found this to be true in the context of the basic radial I_L integrals, where we explored what happens as one goes to higher L values in the formulas discussed above. Comparing the results with $L = 2 \rightarrow 8$, the agreement drops from 30 digits to 20 digits, i.e. a loss of 10 significant digits, for methods two and three, and the agreement with method one is even worse. The remedy for this is to compute in higher precision. Computing the same integrals in quad-double-with exponent (QDE) precision (twice quadruple precision) resulted in > 40 decimal agreement among all three methods. Eq. 20 of Wang, et al. [13], not surprisingly (given the alternating signs, which can lead to loss of digits due to differencing), was the outlier, with the agreement between the recursion formulation and Equation 57 being > 50 decimal places (triple-double agreement) for L up to what is needed for a basis set of STOs including g orbitals, the cases of interest in this work, but differing with the first method only up through 40 decimals. The results are presented in Table I to an accuracy that all three methods agreed upon. All of the calculations in this work were done by the second method, i.e., evaluatng I_0 using Equations 41 and 45 and then using the recursion formula Equation 51 to recur to higher L values, because the same or similar Efros [49] recursion has been used very effectively for He by Korobov [50].

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[20]Table 1 in Wang, et al. [13].

[21]The first three integrals in the table were not computed by the first method since $A(n, \alpha)$ in that formula diverges for n negative.

Table I: Values of the two-electron integral I_L, Equation 57.

N_1	N_2	ω_1	ω_2	ω_{12}	ν	L	I_L
2	2	4.0	2.0	-0.5	1	1	-2.4315 6463 4556 1864 3014 8411 0102 9469 $\times 10^{-2}$
2	2	4.0	2.0	-0.5	2	2	1.6259 9505 7989 0267 9636 0405 3970 0855 $\times 10^{-2}$
3	3	4.0	2.0	-0.5	2	2	9.1050 7686 1404 5610 0986 3201 3893 8688 $\times 10^{-2}$
3	3	4.0	2.0	-0.5	3	3	-8.2953 3899 0777 5777 6928 7467 8058 3731 $\times 10^{-2}$
4	4	4.0	2.0	-0.5	3	3	-8.3506 7423 0967 4160 2817 9419 7851 2615 $\times 10^{-1}$
4	4	4.0	2.0	-0.5	4	4	9.8149 0725 6882 9509 1443 8798 2068 1815 $\times 10^{-1}$
5	5	4.0	2.0	-0.5	4	4	1.5468 4275 4008 7896 5826 5359 6281 5237 31 $\times 10$
5	5	4.0	2.0	-0.5	5	5	-2.2257 7342 1570 2894 3546 4408 1911 0905 28 $\times 10$
6	6	4.0	2.0	-0.5	5	5	-5.0508 7795 2154 7833 1395 5043 0328 2492 25 $\times 10^2$
6	6	4.0	2.0	-0.5	6	6	8.5840 1465 5815 6111 4781 5756 7703 7817 48 $\times 10^2$
7	7	4.0	2.0	-0.5	6	6	2.6518 8706 6861 5185 1907 7403 9393 5256 10 $\times 10^4$
7	7	4.0	2.0	-0.5	7	7	-5.1968 8361 5104 7026 8265 0442 8761 2250 88 $\times 10^4$
8	8	4.0	2.0	-0.5	7	7	-2.0976 2020 1755 4950 1500 3631 9164 8367 83 $\times 10^6$
8	8	4.0	2.0	-0.5	8	8	4.6571 1215 7877 2782 6101 4537 7170 5417 40 $\times 10^6$

D. Exponentially Correlated Calculations and Comparison With Earlier Results

The following calculations were done both to test the codes and to explore the added flexibility brought about by generalizing the linear r_{ij} factor of traditional Hy-CI to the r_{ij} factor of E-Hy-CI, $g(r_{ij}) = r_{ij}^{m} \times e^{-\omega_{ij} r_{ij}^{n}}$, where m,n can take on the following values: {0,0, 0,1, 1,0, 1,1}.

1. Tsein and Pack

The first calculations were a repeat the 1968 calculations of Tsien and Pack [52], which were a one term Exponentially Correlated Slaters (ECS) (exponentially correlated r_{12} only) calculation and a two term linear r_{12} (or classic Hy) calculation whose spacial parts are

$$\Psi_{ECS} = e^{-\omega_1 r_1 - \omega_2 r_2} e^{-\omega_{12} r_{12}} \tag{58}$$

and

$$\Psi_{Hy} = e^{-\omega_1 r_1 - \omega_2 r_2}(1 + c_1 r_{12}), \tag{59}$$

respectively.

Results are tabulated in Table II, which agree with Tsein and Pack to all of the digits they report. Channeling Hirshfelder's suggestion [14] that an exponentially correlated r_{12} paired with a linear r_{12} factor has the right kind of behavior both in the vicinity of the r_{12} cusp as r_{12} goes to 0 and as r_{12} goes to infinity, we extended their work to include both exponential and linear r_{12} terms in the 4 term Exponentially correlated Hy (E-Hy) run whose spacial part is

$$\Psi_{E-Hy} = e^{-\omega_1 r_1 - \omega_2 r_2}(1 + c_1 r_{12} + c_2 e^{-\omega_{12} r_{12}} + c_3 r_{12} e^{-\omega_{12} r_{12}}). \tag{60}$$

From Table II it can be seen that the E-Hy wave function is superior to an Hy wave function by about 0.1 millihartree and to an ECS only wave function by about 1.94 millihartree.

Table II: Comparison of theoretical He ground state nonrelativistic energies (in hartrees). N is the number of terms in the expansion. All energies are variational. All results were obtained in quadruple precision (QP).

Technique	Author	N	ω_1	ω_2	ω_{12}	Energy (hartree)
ECS	Tsein and Pack (1968) [52]	1	1.8581	1.8581	0.2547	-2.8896 18
Hy	Tsein and Pack (1968) [52]	2	1.8497	1.8497	0	-2.8911 21
E-Hy	This work	4	1.8497	1.8497	0.2547	-2.8912 0818
hydrogenic	Bonham and Kohl (1966) [53]	1	1.1885	2.1832		-2.8756 61
Hy	Bonham and Kohl (1966) [53]	2	1.4368	2.2077	0	-2.9014 19
E-Hy	Bonham and Kohl (1966) [53]	2	1.4115	2.2061	0.1016	-2.9019 11
ECS	Bonham and Kohl (1966) [53]	1	1.4096	2.2058	0.2420	-2.9019 23
ECS	Harris and Smith (2005) [54]		2.373427	1.823077	0.190179	
ECS	Harris and Smith (2005) [54]		2.508989	1.767884	0.130308	
ECS	Harris and Smith (2005) [54]		2.068441	2.022821	0.264338	
ECS	Harris and Smith (2005) [54]	4	2.106452	1.395750	-0.96177	-2.9036 88
CI	Sims and Hagstrom (2002) [16]	2743[1]				-2.9036 8919
Hy	Sims and Hagstrom (2002) [16]	100[2]				-2.9037 2281
Hy-CI	Sims and Hagstrom (2002) [16]	1520[3]				-2.9037 2427
E-Hy	This work	8	2.106452	1.395750	-0.96177	-2.9036 8839
E-Hy	This work	12	2.106452	1.395750	-0.96177	-2.9036 8867
ECS	Thakkar and Smith (1977) [15]	10				-2.9037 1318 1
ECS	Thakkar and Smith (1977) [15]	20				-2.9037 2273 0
ECS	Thakkar and Smith (1977) [15]	50				-2.9037 2431 6
ECS	Thakkar and Smith (1977) [15]	60				-2.9037 2435 0
ECS	This work[4]	400				-2.9037 2437 69
Hy-CI	Sims and Hagstrom (2002) [16]	2280[5]				-2.9037 2437 6955
Reference	NN [55], Schwartz [56, 57]					-2.9037 2437 7034

[1]CI terms through kk orbitals ($l = 8$).
[2]Hy-r_{12} terms through $n_{12}^{max} = 4$.
[3]Hy-CI terms through $l_{max} = 1$ (s, p basis sets).
[4]Using Thakkar and Smith's integral transform method.
[5]Hy-CI terms through $l_{max} = 2$ (s, p, d basis sets).

2. Bonham and Kohl

Bonham and Kohl [53] were perhaps the first (in 1966) to test Hirshfelder's conjecture that pairing an exponential r_{12} factor with a linear r_{12} factor might be even more rapidly convergent than either alone. Some of their calculations were repeated and are included in Table II also, where it can be seen that again E-Hy is better than Hy, this time by about 0.5 millihartree, and here with the same number of terms (2). Interestingly, the ECS result is energetically the best, which presumably indicates a more careful optimization.

3. Harris and Smith

In 2005 a remarkable paper appeared by Harris and Smith [54] which is notable for the compactness of the wave function (only 4 terms) as well as the accuracy of the calculation (about 0.034 millihartree). Furthermore each of the 4 terms is a product of $1s$ orbitals times a simple exponential r_{12} factor, which emphasizes the utility of exponential r_{12} correlation versus linear r_{12} factors. For comparison purposes, some CI, Hy, and Hy-CI results of one of the authors [16] are given[22]. The authors [54] do point out that a very careful optimization is needed to obtain this level of compactness and accuracy. The authors also point out that the ω_1, ω_2, and ω_{12} exponential powers do not need to be negative[23], just two out of the three, i.e., they are allowing for positive exponentials as well as negative, and the exponential powers for the first three ω_{12}s are negative (the ωs are positive, the exponential powers are negative). Adding linear r_{12} terms to this wave function has been tested by first adding just linear r_{12} terms to the same 4 $1s$ orbitals used by Harris and Smith, to produce an 8 term wave function[24]. The gain was on the μhartree level, namely,

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[22]The CI result is of comparable accuracy, the Hy and Hy-CI results are more accurate.

[23]corresponding to positive ω_1, ω_2, and ω_{12} values, since ω enters into the exponentials with a negative sign.

[24]Since all four of the Harris and Smith w_{12} values were used, none are listed in the table for either the 8 term wave function or the 12 term wave function which follows it.

0.38 μhartree. Next we added linear r_{12} terms to this 8 terms wave function (hence again channelling Hirshfelder's exponentially correlated r_{12} paired with a linear r_{12} factor) for an additional 0.27 μhartree with a 12 term wave function. The smaller gains here to some extent probably reflect the quality of the Harris and Smith compact wave function.

4. Thakkar and Smith

Exponentially correlated r_{12} was shown by Thakkar and Smith [15] to give very good results for helium-like ions even with rather compact wave functions[25]. The data in their paper was used to repeat their 10 through 50 term calculations with complete agreement (their results are given in Table II). This facilitated the extension of their calculations to 400 terms, thus extending their accuracy from 0.01 μhartree for 66 terms to 0.1 nanohartree for 400 terms. Comparing this 400 term ECS result with the 2280 term Hy-CI expansion needed to achieve a comparable level of accuracy suggests that adding an exponentially correlated r_{12} factor to an Hy-CI wave function might indeed hasten convergence. This is explored in the next section by carrying out detailed E-Hy-CI calculations and comparing them with the same Hy-CI calculations without the exponentially correlated r_{12} factor.

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[25]0.01 μ h energy for He with 66 terms.

IV. Comparison of E-Hy-CI and Hy-CI

In earlier work on the ground state of He, one of the authors [16] built up an Hy-CI wave function by progressively adding in higher angular momentum basis sets, in what might be referred to as s-wave, p-wave, ..., out to and including j-wave ($l = 7$) sets times both 1 and r_{12}. In the present work a similar approach for E-Hy-CI facilitates a comparison of E-Hy-CI and Hy-CI. The earlier work was greatly influenced by the work of Drake [58], who pointed out the need for "doubling" basis sets so there is a natural partition of the basis set into two distinct distance scales - one appropriate to the complex correlated motion near the nucleus, and the other appropriate further out[26]. This observation will prove convenient in analyzing the results of the E-Hy-CI and Hy-CI results tabulated in Table III. This work builds on the work of another one of the authors, Ruiz (2015), who uses just one basis set and also provides energy limits for s-wave, p-wave, d-wave and f-wave Hy-CI 'limits'. Drake uses just two sets of orbitals to accelerate convergence, Sims and Hagstrom used two sets of basis functions for each l, differing in the nonlinear parameters ξ and η, and Ruiz used just one set of basis functions. In the "double" basis set Hy-CI, the first set has an orbital with an orbital exponent $\xi = \eta$ that makes it essentially a valence shell orbital similar to the Ruiz outer (valence) shell orbital, whereas for the second set ($\xi = \eta$ again), the orbital has a large exponent which brings it in closer to the nucleus.

1. E-Hy-CI vs. Hy-CI using a single basis set of orbitals

To clarify this further, consider Table III, where the basis sets for both of the Hy-CI calculations as well as the new E-Hy-CI calculation are listed. Each line in the table specifies the {inner,inner} and {outer,outer} sets for each l quantum number ($= l_{max}$). In the table, only the minimum information needed to specify the basis set is listed, namely, an

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[26]For a good review, see [59], where Drake says that "doubling" the basis set leads to a dramatic improvement in accuracy.

exponent ζ ($\xi = \eta = \zeta$), the l quantum number for orbitals with that exponent, n_{orbs}, the number of orbitals with that exponent (the n_i in Equation 5 run from l_i to $n_{orbs} + l_i - 1$), and ω_{12}, the exponent of the exponentially correlated r_{12} factor if this is an E-Hy-CI calculation. There is of course just one n_{orbs} for the single basis set Hy-CI calculations and an outer n_{orbs} and inner n'_{orbs} basis set for double basis sets. In all of the tables, N is used to refer to the number of terms in the wave function (see Equation 3).

In examining the table, the first thing that stands out is how easy it was to get a result orders of magnitude better than the s-wave set 'limit' for Hy-CI, the 760 term result of [16]. Using just the 90 term s-wave set Hy-CI of [9], and taking an additional 90 terms, each term now also containing an exponentially correlated $\mathrm{e}^{-\omega_{12}\mathrm{r}_{12}}$ factor whose exponent ω_{12} is chosen to be the one (0.5) which satisfies the Kato cusp condition, we get an 180 term E-Hy-CI wave function result that is orders of magnitude better than the s-wave limit for Hy-CI, and it is even better than the 1520 term p-wave Hy-CI limit. The best s-wave set E-Hy-CI 840 term result is even pushing the [16] d-wave set 2280 term Hy-CI limit; the best single basis p-wave set E-Hy-CI result, obtained by taking the Ruiz 800 p-wave set Hy-CI and adding another 800 terms with $\mathrm{e}^{-\omega_{12}\mathrm{r}_{12}}$ for an 1600 term E-Hy-CI wave function, is substantially better than this limit. Continuing in this fashion to d and f single basis sets yields diminishing returns, in line with what Sims and Hagstrom found in their previous CI, Hy, and Hy-CI study of this state.

Sims and Hagstrom found the surprising result that one simply can't get to their answer without the {inner,inner} terms without a really massive increase in the expansion length. Many authors, starting perhaps with Roothaan and Weiss [41], have emphasized that the wave function should have a cusp-like behavior at $r_{12} = 0$ such that

$$\left(\frac{1}{\Psi} \frac{\partial \Psi}{\partial r_{12}} \right)_{r_{12}=0} = \frac{1}{2} \tag{61}$$

and attributed the slow CI convergence to the necessity of piling up higher $s, p, d, ...$ angular terms in attempting to represent the details of this behavior. However no one had emphasized the need for {inner,inner} terms at higher l values. As pointed out in [16], if one drops the {inner,inner} terms from the expansion in the last line of Table 1 and keeps all orbital exponents fixed, the result is E(2324 terms) = -2.9037 2437 7026 hartree, which is not as good as the results Frankowski and Pekeris [60, 61] obtained in 1966. What this suggests is that -2.9037 2437 7026 hartree is about the limit of a single basis set Hy-CI for He, which would suggest that the Ruiz 1584 term Hy-CI result will converge very slowly from here on. What the E-Hy-CI result shows is that that inner region defect can be overcome by the simple expedient of augmenting the Hy-CI calculation with an exponentially

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correlated basis just as has been done here, to picohartree accuracy.

Table III: Comparison of theoretical E-Hy-CI and Hy-CI energies for the He ground state (in hartrees). All energies are variational; all calculations were done in quadruple-double-with exponent (QDE) precision.

Technique	Author	l_{max}	n_{orbs}	ξ	n'_{orbs}	ξ'	ω_{12}	N	Energy (hartree)
Hy-CI	Ruiz (2015) [9]	0	9	2.9814				90	-2.9034 9650 6178 4873
Hy-CI	Ruiz (2015) [9]	0	20	2.9814				420	-2.9034 9813 3768 2647 9878
Hy-CI	SH (2002) [16]	0	19	2.20	19	25.0		760	-2.9034 9832 0585 8801 1976 9235
E-Hy-CI	This work	0	9	2.9814			0.5	180	-2.9037 2430 0278 5830 7962 8670
E-Hy-CI	This work	0	20	2.9814			0.5	840	-2.9037 2435 3896 0173 3543 8052
Hy-CI	Ruiz (2015) [9]	1	19	2.9814				800	-2.9037 2426 7864 5688 1088
Hy-CI	SH (2002) [16]	1	19	3.05	19	40.5		1520	-2.9037 2426 8354 6045 9864 6392
E-Hy-CI	This work	1	19	2.9814			0.5	1600	-2.9037 2437 7033 2396 1091 0167
Hy-CI	Ruiz (2015) [9]	2	18	2.9814				1142	-2.9037 2437 6943 7414 6155
Hy-CI	SH (2002) [16]	2	19	3.50	19	40.5		2280	-2.9037 2437 6954 6918 8919 8809
E-Hy-CI	This work	2	18	2.9814			0.5	2284	-2.9037 2437 7033 6475 6471 0855
Hy-CI	Ruiz (2015) [9]	3	17	2.9814				1452	-2.9037 2437 7024 3236 8211
Hy-CI	SH (2002) [16]	7	13	6.50				2324	-2.9037 2437 7026
E-Hy-CI	This work	3	17	2.9814			0.5	2896	-2.9037 2437 7033 8188 1906 3208
Hy-CI	SH (2002) [16]	3	18	3.90	18	40.5		2964	-2.9037 2437 7034 0541 4170 4466
Hy-CI	SH (2002) [16]	4	15	4.50	15	40.5		3444	-2.9037 2437 7034 1195 3899 2122
Hy-CI	SH (2002) [16]	5	14	5.20	14	40.5		3864	-2.9037 2437 7034 1195 9822 0159
Hy-CI	SH (2002) [16]	6	14	6.00	14	40.5		4284	-2.9037 2437 7034 1195 9829 6249
Reference[1]									-2.9037 2437 7034 1195 9831 1159

[1]Nakashima and Nakatsuji (2007) [55], Schwartz (2006) [56, 57].

2. E-Hy-CI vs. Hy-CI using a different doubled basis set for each different l-wave

Including both {inner,inner} and {outer,outer} terms was key to the success of the current Hy-CI formalism in the 2002 study [16]. The effect of converting those "doubled" basis set Hy-CI wave functions into "doubled" basis set E-Hy-CI wave functions is explored in this section using the same simple procedure used in the previous section: for each term in the wave function, add to the wave function a term now also containing an exponentially correlated $e^{-\omega_{12}r_{12}}$ factor whose exponent ω_{12} is chosen to be the same (0.5) which satisfies the Kato cusp condition. The results are tabulated in Table IV, where very dramatic improvements can be seen:

- Hy-CI s-wave 3 decimal place accuracy becomes 7 decimal place E-Hy-CI s-wave accuracy ($>$ Hy-CI p-wave accuracy),

- Hy-CI p-wave 6 decimal place accuracy becomes 13 decimal place E-Hy-CI p-wave accuracy ($>$ Hy-CI f-wave accuracy),

- Hy-CI d-wave 8 decimal place accuracy becomes 18 decimal place E-Hy-CI d-wave accuracy ($>$ Hy-CI g-wave accuracy), a huge 10 decimal place improvement,

- Hy-CI f-wave 12 decimal place accuracy becomes 19 decimal place E-Hy-CI accuracy ($>$ Hy-CI $l = 6$ accuracy).

- from here on convergence gets slower, but already at the E-Hy-CI f-wave expansion the result is almost as good as the $l = 10$ limit Hy-CI expansion which is a new Hy-CI limit.

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Table IV: Comparison of theoretical E-Hy-CI and Hy-CI energies for the He ground state (in hartrees) using a doubled basis set of orbitals for each l-wave). All energies are variational; all calculations were done in quadruple-double-with exponent (QDE) precision.

Technique	Author	l_{max}	n_{orbs}	ξ	n'_{orbs}	ξ'	ω_{12}	N	Energy (hartree)
Hy-CI	SH (2002) [16]	0	19	2.20	19	25.0		760	-2.9034 9832 0585 8801 1976 9235
E-Hy-CI	This work	0	19	2.20	19	25.0	0.5	1520	-2.9037 2435 4275 7390 6714 2971
Hy-CI	SH (2002) [16]	1	19	3.05	19	40.5		1520	-2.9037 2426 8354 6045 9864 6392
E-Hy-CI	This work	1	19	3.05	19	40.5	0.5	3040	-2.9037 2437 7034 1043 9282 0252
Hy-CI	SH (2002) [16]	2	19	3.50	19	40.5		2280	-2.9037 2437 6954 6918 8919 8809
E-Hy-CI	This work	2	19	3.50	19	40.5	0.5	4560	-2.9037 2437 7034 1195 9808 7177
Hy-CI	SH (2002) [16]	3	18	3.90	18	40.5		2964	-2.9037 2437 7034 0541 4170 4466
E-Hy-CI	This work	3	18	3.90	18	40.5	0.5	5928	-2.9037 2437 7034 1195 9830 8206
Hy-CI	SH (2002) [16]	4	15	4.50	15	40.5		3444	-2.9037 2437 7034 1195 3899 2122
E-Hy-CI	This work	4	15	4.50	15	40.5	0.5	6888	-2.9037 2437 7034 1195 9830 8900
Hy-CI	SH (2002) [16]	5	14	5.20	14	40.5		3864	-2.9037 2437 7034 1195 9822 0159
E-Hy-CI	This work	5	14	5.20	15	40.5	0.5	7728	-2.9037 2437 7034 1195 9830 9216
Hy-CI	SH (2002) [16]	6	14	6.00	14	40.5		4284	-2.9037 2437 7034 1195 9829 6249
E-Hy-CI	This work	6	14	6.00	14	40.5	0.5	8568	-2.9037 2437 7034 1195 9830 9368
E-Hy	AZ (2015) [50]							3000	-2.9037 2437 7034 1195 9831
Hy-CI	This work	10	9	8.50	9	36.5		6160	-2.9037 2437 7034 1195 9831 0465
ECS	KO (2002) [62]							5200	-2.9037 2437 7034 1195 9831 1158
Reference[1]									-2.9037 2437 7034 1195 9831 1159

[1]Nakashima and Nakatsuji (2007) [55], Schwartz (2006) [56, 57].

From the table it can be seen that ECS, E-Hy, Hy-CI and E-Hy-CI are all capable of greater than 20 decimal place accuracy for two electrons, with the Hy-CI 6160 term wave function being a by-product of this research. In the next section successive l-wave expansions for for the 6160 term wave function through $l = 6$ are used to do some limited exploration of the effect of varying ω_{12} and final results are presented.

3. Optimization of ω_{12}

For the final runs the basis orbitals were re-optimized after increasing the number of orbitals to n_{orbs} = 19 for l = 0 through 5, and 15 for l = 6. In Table V the first line for each l is the unoptimized result and the second the optimized result. It can be seen that the {inner,inner} set orbital exponents don't change much, and while there are big changes for l = 1 and l = 2, after that not so much. This is consistent with earlier experience that the energy contributions are fairly insensitive to the orbital exponent and depend much more on the number of orbitals (power of r), the reason for the increase in n_{orbs}. For each block (N), the exponential orbital exponent ω_{12} was kept at the 0.5 Kato cusp condition value for the first calculation, whereas for the second calculation Energy was optimized with respect to ω_{12}. One can see a fairly substantial increase in energy resulting from optimizing at both the l = 0 and l = 1 level. At l = 1 the energy curve turned out to be fairly flat over a wide range of values, so for $l \geq 2$ ω_{12} was fixed at 1.83. Our final result, -2.9037 2437 7034 1195 9831 1084 hartree, is better than all previous calculations except for the ECS calculation of Korobov [62] (in which he generates and optimizes thousands of non-linear parameters) and the landmark 40 and 45 decimal calculations of Nakashima and Nakatsuji [55] and Schwartz [56, 57] respectively.

Table V: The effect of optimization of ω_{12} for the $1\ {}^1S$ He ground state (in hartrees). All energies are variational; all calculations were done in quadruple-double-with exponent (QDE) precision.

Technique	Author	l_{max}	n_{orbs}	ξ	n'_{orbs}	ξ'	ω_{12}	N	Energy (hartree)
E-Hy-CI	This work	0	19	2.20	19	25.0	0.5	1520	-2.9037 2435 4275 7390 6714 2971
E-Hy-CI	This work	0	19	2.14	19	25.5	0.701	1520	-2.9037 2435 8492 3200 2465 7719
E-Hy-CI	This work	1	19	3.05	19	40.5	0.5	3040	-2.9037 2437 7034 1043 9282 0252
E-Hy-CI	This work	1	19	3.04	19	68.5	1.83	3040	-2.9037 2437 7034 1176 9396 9022
E-Hy-CI	This work	2	19	3.50	19	40.5	0.5	4560	-2.9037 2437 7034 1195 9808 7177
E-Hy-CI	This work	2	19	3.55	19	56.5	1.83	4560	-2.9037 2437 7034 1195 9823 8090
E-Hy-CI	This work	3	19	3.90	19	40.5	0.5	6080	-2.9037 2437 7034 1195 9830 7934
E-Hy-CI	This work	3	19	3.95	19	36.5	1.83	6080	-2.9037 2437 7034 1195 9831 0960
E-Hy-CI	This work	4	19	4.50	19	40.5	0.5	7600	-2.9037 2437 7034 1195 9831 1049
E-Hy-CI	This work	4	19	4.60	19	36.5	1.83	7600	-2.9037 2437 7034 1195 9831 1056
E-Hy-CI	This work	5	19	5.20	19	40.5	0.5	9120	-2.9037 2437 7034 1195 9831 1065
E-Hy-CI	This work	5	19	5.25	19	36.5	1.83	9120	-2.9037 2437 7034 1195 9831 1077
E-Hy-CI	This work	6	15	6.00	15	40.5	0.5	10080	-2.9037 2437 7034 1195 9831 1073
E-Hy-CI	This work	6	15	5.90	15	36.5	1.83	10080	-2.9037 2437 7034 1195 9831 1084
ECS	KO (2002) [62]							5200	-2.9037 2437 7034 1195 9831 1158
Reference[1]									-2.9037 2437 7034 1195 9831 1159

[1]Nakashima and Nakatsuji (2007) [55], Schwartz (2006) [56, 57].

V. Conclusion

The renewed interest in explicitly correlated wave functions these days is coming from the incredible accuracy of experiments these days. To do as well theoretically requires explicitly correlated wave functions, as can be seen from Table VI. One of these methods, Hy-CI, has been shown to be able to produce picohartree accuracy relatively easily [9] for two-electron atoms, and has been utilized to produce high precision results for not only ground states but excited states as well for two-, three- and four-electron atoms and ions. Fundamental to the method is the restriction of one r_{ij} per CSF, which has achieved 10 - 20 nanohartree accuracy for the ground states of the Be isoelectronic series with Z$\geq$ 4 and for excited states of Be. For both extension of the method to N$>$ 4 as well as for excited states of two-four electron systems, speeding up the convergence of the method needs to be studied. By comparing convergence of the E-Hy-CI wave function expansion to that of the Hy-CI wave function without exponential correlation factors, both convergence acceleration and an improvement in the accuracy for the same basis are demonstrated. While ultimately the E-Hy-CI convergence resembles that of Hy-CI[27], it is the very dramatic convergence improvements of $s-$, $p-$, $d-$ and f-wave E-Hy-CI expansions compared to the Hy-CI l-wave expansions that is important, because it offers a way of overcoming the ultimately slow convergence of 'the $r_{12}r_{34}$' double cusp, analogous to the r_{12} cusp problem for CI, that arises for N $\geq$ 4 electron systems. This makes the application of the E-Hy-CI method to systems with $N > 4$, for which this formalism with at most a single $r_{ij}^{\nu_{ij}} e^{-\omega_{ij} r_{ij}}$ factor per term leads to solvable integrals[28], very promising.

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[27]The $l = 6$ E-Hy-CI result is however superior to the $l = 10$ result for Hy-CI.

[28]Hy-CI and its extension to E-Hy-CI are unique in this regard.

Table VI: Comparison of theoretical He ground state nonrelativistic energies (in hartrees).
N is the number of terms in the expansion. All energies are variational.

Technique	Author	N	Energy (hartree)
	Frankowski and Pekeris (1966) [60, 61]	246	-2.9037 2437 7032 6
	Freund, Huxtable and Morgan (1984) [63]	230	-2.9037 2437 7034 0
ECS	Thakkar and Koga (1994) [64]	308	-2.9037 2437 7034 1144
	Goldman (1998) [65]	8066	-2.9037 2437 7034 1195 9382
Hy	Drake (1999) [58]	2114	-2.9037 2437 7034 1195 9582
ECS	Korobov (2000) [66]	2200	-2.9037 2437 7034 1195 9829 55
Hy	Drake, Cassar and Nistor (2002) [67]	2358	-2.9037 2437 7034 1195 9830 5
Hy-CI	This work (2020)	6160	-2.9037 2437 7034 1195 9831 0465
E-Hy-CI	This work (2020)	10080	-2.9037 2437 7034 1195 9831 1084
ECS	Korobov (2002) [62]	5200	-2.9037 2437 7034 1195 9831 1158
Reference[1]			-2.9037 2437 7034 1195 9831 1159

[1]Nakashima and Nakatsuji (2007) [55], Schwartz (2006) [56, 57].

One other possible avenue of convergence acceleration of the method is to explore another extension to the method, an introduction of unlinked r_{ij} pairs into the method to handle the ultimately slow convergence of 'the $r_{12}r_{34}$' double cusp. It is possible that E-Hy-CI will obviate the need for this extension, and if so it will be better than unlinked pairs because that ansatz requires 5 and 6 electron integrals, whereas E-Hy-CI, like Hy-CI, has at most 4 electron integrals. To answer this question as well as to see how well the E-Hy-CI extension works in general, there needs to be an E-Hy-CI calculation on a four-electron system[29], which would be a natural extension of the work done herein.

E-Hy-CI method variational calculations with up to 10080 expansion terms are reported for the ground ^1S state of the neutral helium atom, with a resultant nonrelativistic energy of -2.9037 2437 7034 1195 9831 1084 nanohartree for the best expansion.

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[29]Previous experience with Li suggests that the linked product terms $r_{ij}r_{ik}$ shouldn't be expected to give problems until the nanohartree level, but this could be investigated in a four-electron E-Hy-CI calculation as well.

Acknowledgments

Appendix. $\Gamma_{-1,m,n}(\alpha, \beta, \gamma)$

For this case, the starting formula is

$$\Gamma_{-1,0,0}(\alpha, \beta, \gamma) = \frac{\{\ln(\alpha + \beta) - \ln(\alpha + \gamma)\}}{\beta^2 - \gamma^2} \tag{A1}$$

and the recurrence relations, valid when $\beta - \gamma$ is not too small, are [43]

$$\Gamma_{-1,m,n} = \frac{1}{\beta + \gamma} \left[m\Gamma_{-1,m-1,n} + n\Gamma_{-1,m,n-1} + G_{m,n} \right], \tag{A2}$$

$$G_{mn} = \frac{1}{\beta - \gamma} \left[mG_{m-1,n} - nG_{m,n-1} + K_{mn} \right], \tag{A3}$$

$$K_{mn} = \delta_{m,0}\, \delta_{n,0} \ln(\frac{(\alpha + \beta)}{(\alpha + \gamma)}) - \frac{\delta_{n,0}(1 - \delta_{m,0})(m - 1)!}{(\alpha + \beta)^m} \\ + \frac{\delta_{m,0}(1 - \delta_{n,0})(n - 1)!}{(\alpha + \gamma)^n} \tag{A4}$$

where $\Gamma_{-1,m,n}$, $G_{m,n}$ and $K_{m,n}$ are abbreviated in a manner similar to what has done before. It is clear from Equation A3 that if $\beta - \gamma$ is too small, the recursion will be unstable. When $\beta - \gamma$ is not too small the recursion can be done in a computationally fast and stable fashion by evaluating the array K first, then G, then Γ.

For $\beta - \gamma$ small, following Harris [42, 43] $x = \frac{1}{2}(\beta + \gamma)$ and $y = \frac{1}{2}(\beta - \gamma)$ are introduced in $G_{0,0}$ such that

$$G_{0,0} = \frac{\ln(\alpha + x + y) - ln(\alpha + x - y)}{2y}. \tag{A5}$$

Then expand Equation A5 in the power-series expansion

$$G_{0,0} = \sum_{k=0}^{\infty} \frac{y^{2k}}{(2k + 1)(\alpha + x)^{2k+1}} \tag{A6}$$

and differentiate with respect to β and γ to obtain the result

$$G_{m,n} = \frac{m!}{(\alpha+\beta)^{m+n+1}} \sum_{k=0}^{\infty} \frac{(n+k)! y^k}{k!(m+n+k+1)} \qquad (A7)$$

which replaces Equation A3.

As a check on the coding of this case, the calculation of $G_{2,3}$ of Harris [43] was repeated, and complete agreement with his 'Exact result' result was obtained to the number of digits reported in the table.

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