CHAPTER NINE

High-precision Hy-CI and E-Hy-CI studies of atomic and molecular properties

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Abstract

This review presents a survey of the most important achievements in atomic and molecular calculations obtained with the Hylleraas-configuration interaction method (Hy-CI) and its extension, the exponentially correlated Hylleraas-configuration interaction method (E-Hy-CI), explaining what led to it and discussing the main mathematical and computational issues. We stress the importance of representing the electronic cusp well in the wave function, which a configuration interaction (CI) wave function does not

do, along with the shortcomings of other implicitly correlated wave functions with respect to this cusp. There follows a short review of the types of explicitly correlated wave functions, culminating with an exploration of a generalization of the Hy-CI first proposed in a previous study, 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 $r_{ij}^{\nu_{ij}} e^{-\omega_{ij} r_{ij}}$. We include (1) atomic calculations on states of the He through B atoms using the Hy-CI method, including atomic spectra and isoelectronic ions and the first atomic calculations on the ground state of the He atom employing the E-Hy-CI method, (2) molecular calculations by the Hy-CI method of the H_2 molecule using both Slater-type and Gaussian-type orbitals, and (3) calculations of various atomic and molecular properties beyond the energy.
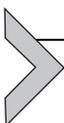
1. Introduction

Today we are witnessing the dawn of a new era in computational Quantum Chemistry, accompanied by the use of basis sets of increasing size on increasingly powerful computers. However, as basis sets of larger size are devised, numerical problems become much more acute on machines that have a finite word length. Practical linear dependence problems arise, which must be controlled to maintain precision. The need to avoid computational linear dependence is the key issue in constructing the large basis sets required for accurate electronic studies utilizing the variational method. The solution to the linear dependence problem is always to increase the precision of the arithmetic, which in turn leads to higher CPU costs. The use of thousands or more terms in a wave function also leads to memory problems arising from storage of the matrix elements prior to the matrix diagonalization step. It is these higher CPU costs and larger memory requirements, combined with the exponential growth of the number of terms that have to be included to maintain precision as N (the number of electrons) increases, which have led some to a very pessimistic view of the possibilities for extending the phenomenal success of high–precision calculations for He (N = 2) to atoms of more than three electrons. For example, in a review article on Computational Chemistry in 1996, Clementi and Corongiu[1] stated that using an Hy–CI expansion to solve the dynamical correlation is nearly impossible for more than three or four electrons.

Today, however, cheap CPUs can be connected in parallel to enhance (by orders of magnitude) both the CPU power and the memory that can be brought to bear on the computational task. Techniques that appeared hope–less only a few years ago are now plausible, assuming the linear dependence

problem can be obviated with extended precision. All of the above has led to a re-examination of methods which are known to give the most accurate upper bounds to energy states, in the hope that high precision measurement of atomic properties with the computer will extend from He to Li, from Li to Be, from Be to B and beyond. The work begun by Clementi and coworkers on diatomic molecules can hopefully be extended to systems with more than four electrons.

The Schrödinger equation and the relativistic Dirac-Coulomb equation are the basic principles governing chemistry and related sciences. However, the fact that these equations have dependent variables prevented computation of accurate numerical solutions until the past two decades. The difficulty is that electrons interact dynamically (simultaneously) and their motion is *correlated*. This is the *many body problem* at the heart of chemistry.

In 1929 Egil Hylleraas[2] was able to compute the energy of the ground state of the He atom to millihartree precision, obtaining an energy of –2.90324 hartree. In that work Hylleraas wrote: "*It is then quite clear for me, that here if the extreme limit of capability in these calculations would be achieved, the exact treatment of more difficult systems would be hopeless. (…) I have finally succeeded to find a method, that for helium leads to the desired results and hopefully will prove to be fruitful also for other problems.*"

The key to Hylleraas' success was the direct inclusion of the interelectronic coordinate r_{12} in the wave function. The Hylleraas (Hy or Hy-r_{ij}) method is perhaps best exemplified by the work of Drake and collaborators.[3–7] It uses factors of powers of r_{ij} in the wave function and has by now been extended to the point that it is possible to calculate *essentially exact for all practical purposes* nonrelativistic energies for helium (He) and other three body systems. This review will show how methodology based on the ideas of Hylleraas enables us to go beyond He and determine energies and properties of ground and excited states of light atoms and small molecules to high precision.

1.1 Importance of the cusp in the wave function

Much of our treatment of many electron systems is based on solutions to one-electron systems such as atomic hydrogen (H) and molecular H_2^+, the familiar s, p, d, … atomic orbitals and their molecular counterparts. Many authors, starting perhaps with Roothaan and Weiss,[8] have emphasized that the wave function should vanish as the electron separation r_{ij} goes to 0, for any two electrons i and j. A strictly orbital picture cannot accurately represent this cusp-like behavior. We need wave functions which show a
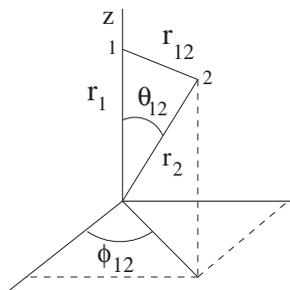
Fig. 1 Definition and rotation of the coordinates of two electrons about an atomic center.

correct cusp when the distance between electrons is close to zero, and also decay correctly when the distance between the electrons goes to infinity.

The distance r_{12} between electrons 1 and 2 is illustrated in Fig. 1 in a polar coordinate system.

Expressed mathematically, for arbitrary electrons i and j, the equation of the electronic cusp condition, where r_{ij} is the distance between electrons i and j, is[a]

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

Wave functions which contain linear r_{ij} terms, including Hy wave functions, fulfill the cusp condition and converge rapidly to the exact solution, whereas orbital-based methods such as CI (for reviews of CI methods, see Ref. 10, 11) do not. To show this as well as the connection between these methods, we give an example using He calculations. Without going into detail, an Hy-CI wave function for the ^1S ground state of He can be expressed as[12]

$$\Psi = \sum_K C_K \Phi_K, \tag{2}$$

where the C_K are the variationally determined expansion coefficients, and the basis functions Φ_K are of the form

$$\Phi_K(\mathbf{r}_1, \mathbf{r}_2) = (1 \pm P_{12}) r_1^i r_2^j r_{12}^k P_l(cos\theta_{12}) e^{-\xi r_1 - \eta r_2}, \tag{3}$$

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[a] For a detailed derivation of the conditions on the behavior of a wave function for a system of charged particles near the coalescence of any two of them, see Ref. 9.

where P_{12} permutes electrons 1 and 2 (which is required for symmetry) and $P_l(cos\theta_{12})$ is a Legendre polynomial.[13] Note that the Legendre polynomials in Eq. (3) can be expressed in terms of spherical harmonics[13] of (θ_1, ϕ_1) and (θ_2, ϕ_2) by the spherical harmonic addition theorem[14]:

$$P_l(cos\theta_{12}) = \frac{4\pi}{(2l+1)} \sum_{m=-l}^{l} Y_l^{m*}(1)Y_l^m(2). \tag{4}$$

Substituting this expression in Eq. (3) and taking $k = 0$ gives a conventional CI configuration for S states. There is also a close relationship between our (Hy-CI) wave function and Hy wave functions. Since

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1r_2P_1(cos\theta_{12}), \tag{5}$$

r_{12}^k for $k > 1$, when expanded, gives a polynomial in powers of $P_l(cos\theta_{12})$ times 1 or r_{12} depending on whether k is even or odd. The powers of r_{12} can in turn be expressed in terms of the $P_l(cos\theta_{12})$ polynomials, thus making the connection between Hy and Hy-CI explicit. Although other (radial) factors will be different in the two methods, they are essentially equivalent methods for He, but not for N > 2. Since spherical harmonics contain the angular parts of orbitals and these are proportional to even powers of r_{12} in Eq. (5), a CI wave function and similar *ab-initio* wave functions include implicitly even power terms r_{ij}^2, r_{ij}^4, ... but no linear r_{ij} terms and do not satisfy the cusp condition.

A detailed comparison of Hy, Hy-CI, and CI was done for the ^{1}S ground state of the He atom by Sims and Hagstrom.[12] Table 1 summarizes the CI calculations and includes from *ss* to *xx* orbital excitations where one can see the piling up of orbitals of increasing angular momentum in an attempt to represent the term r_{12} in a Taylor series expansion. The slow (but smooth) convergence of the CI wave function is apparent from the table, especially when compared with a comparable Hy-CI[12] calculation which is more than 14 decimal places better, which led the authors of the study to comment at the time that "After 70 years of trying, the best CI treatment for He is still accurate to only 5 decimal places!".

Wave functions which follow Hylleraas by incorporating terms containing r_{ij} are today known as explicitly correlated wave functions. Of these wave functions, the exponentially correlated ones with terms containing exponential factors of Slater-type $e^{-\alpha r_{ij}}$ lead to a constant when Eq. (1) is applied to the exponential factors, and hence fulfill the cusp condition. In contrast, application of Eq. (1) to the terms of exponentially correlated wave

Table 1 Configuration interaction (CI) calculations on the ^{1}S ground state of the He atom.[12]

N	n	Type	E (hartree)	ΔE (μh)
470	21	ss	**–2.**879 028 756 5	
854	21	pp	**–2.90**0 516 219 9	–21487.5
1221	21	dd	**–2.90**2 766 805 3	–2250.6
1588	21	ff	**–2.903** 321 016 2	–554.2
1819	21	gg	**–2.903** 518 464 9	–197.4
2050	21	hh	**–2.903** 605 515 1	–87.1
2281	21	ii	**–2.903** 649 644 2	–44.1
2512	21	kk	**–2.903** 674 327 6	–24.7
2743	21	ll	**–2.903** 689 193 4	–14.9
2974	21	mm	**–2.903** 698 656 3	–9.5
3184	21	nn	**–2.903 7**04 973 8	–6.3
3415	20	oo	**–2.903 7**09 324 8	–4.4
3625	20	qq	**–2.903 7**12 433 2	–3.1
3835	20	rr	**–2.903 7**14 703 4	–2.3
4045	20	tt	**–2.903 7**16 405 6	–1.7
4255	20	uu	**–2.903 7**17 699 2	–1.3
4426	18	vv	**–2.903 7**18 695 6	–1.0
4579	17	ww	**–2.903 7**19 480 4	–0.8
4699	15	xx	**–2.903 72**0 091 9	–0.6
Exact[20–22]			**–2.903 724 377 034 …**	–4.3

N is the number of configurations, n is the maximum principal quantum number of the orbitals employed, and the orbital type is given (orbital types from Ref. 12 are corrected to use proper spectroscopic notation). E is the nonrelativistic energy.

functions with terms containing exponential factors of Gaussian-type $e^{-\alpha r_{ij}^2}$ do not lead to terms which go to zero as r_{ij} goes to zero. Hence explicitly correlated Gaussian (ECG) wave functions, perhaps best exemplified by the work of Adamowicz and collaborators,[15,16] have an error in addition to the inherent finite basis set truncation error. However, some progress toward alleviating this problem has been made by Pachucki and Komasa.[17,18]

They add terms linear in r_i and r_{ij} to an ECG calculation to produce what they call an LECG (Linear ECG) basis. Even without this correction, Puchalski et al.[19] have achieved nanohartree precision for the four-electron beryllium atom.

In fact both electronic and analogous nuclear cusp conditions should be fulfilled. This is the case for Slater-type orbitals (STOs),[b] but not when using Gaussian–type orbitals (GTOs). There are also three particle coalescence conditions and higher order conditions (for further information, see cusp conditions and energy convergence of the wave functions in Refs. 23, 24). Perhaps because of the electronic cusp condition, variational methods based on explicitly correlated wave functions (including r_{ij} terms) are known to give the most accurate upper bounds to energy states and the inclusion of r_{ij} terms 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[25]). Hy-CI in its current form uses only linear terms in r_{ij}, hence R12/F12[23,25–27] methods are related to Hy-CI beyond the scope of this study (but see Ruiz[24] for a discussion of CI-R12 and a comparison with Hy-CI in the two–electron He atom case).[c]
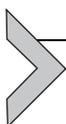
2. High-precision methodology

Table 2 compares each of these methods for atoms up to and including $N = 6$ with the best CI calculations for these systems, which for systems other than He are those of Bunge and collaborators[29–31] employing Bunge's selected CI calculations containing millions of Slater determinants. The methods are presented in order of precision of the calculated He ground state energy.

Of special note are ECG wave functions, whose terms, as mentioned previously, contain exponential factors of Gaussian-type $e^{-\alpha r_{ij}^2}$. For $N > 2$, the terms contain products of these factors which include all interelectronic coordinates at the same time, so the form of the wave function with respect to the interelectronic coordinates is

$$\Psi_{ECG} = \Psi\big(e^{-r_{ij}^2}, e^{-r_{kl}^2}, e^{-r_{mn}^2}\big). \tag{6}$$

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[b] The STOs we use are defined fully in Ref. 13. An s STO has $l = 0$, a p STO has $l = 1$, a d STO has $l = 2$, etc.

[c] Due to the approximations within the R12 method, the energy computed (even with CI-R12) no longer is an upper bound to the exact value.[28]

Table 2 Precision (hartree) of the best variational CI and explicitly correlated methods for each atomic state.

Method	He	H_2	Li	Be	B	C
CI	10^{-5} [12]	10^{-3} [32]	10^{-4} [29]	10^{-4} [30]	10^{-3} [31]	10^{-2} [33]
ECG	10^{-11} [34]	10^{-12} [35]	10^{-9} [36]	10^{-6} [16]	10^{-3} [37]	10^{-2} [38]
Hy	10^{-19} [6]	10^{-12} [39]	10^{-12} [7]	10^{-5} [40]	X	X
Hy-CI	10^{-20} [12]	10^{-12} [41]	10^{-9} [42]	10^{-6} [43]	10^{-1} [44]	
E-Hy-CI	10^{-21} [45]					
ECS	10^{-23} [46]	10^{-12} [47]	10^{-12} [48]	X	X	X
E-Hy	10^{-34} [49]			X	X	X
ICI	10^{-40} [22]	10^{-11} [50]	X	X	X	X
Analytical[a]	10^{-43} [20,21]		X	X	X	X

[a]Reference energy of He ^{1}S ground state: $E = -2.90372\ 43770\ 34119\ 59831\ 11592\ 45194\ 40444\ 66969\ 25310\ 5$ hartree.[20,21]
Estimated reference energy for the ^{2}S ground state of the Li atom: -7.478 060 323 910 147(1) hartree[7] and -7.478 060 323 910 2(2) hartree.[51]
Estimated reference energy for the ^{1}S ground state of the Be atom: -14.667 356 508(1) hartree.[16]
Estimated reference energy for the ^{2}P ground state of the B atom: -24.653 91 hartree.[52]
Estimated reference energy for the ^{3}P ground state of the C atom: -37.845 0 hartree.[52]
Estimated reference energy for the $^1\Sigma_g^+$ ground state of the H_2 molecule: -1.174 475 931 400 216 7(3) hartree.[39]
Blank spaces mean the corresponding calculation has not been done yet whereas Xs signify that the calculations cannot be done with the method without restrictions (see text).

Use of Gaussian-type orbitals leads to easier N-electron integrals, including molecular ones, but suffers from the same inability to represent the electron cusp behavior at $r_{ij} = 0$ as does a strictly orbital CI picture, which is perhaps the reason for the optimization of thousands of parameters in a typical calculation. Still the observed precision is very high, ranging from beyond picohartree precision in the H_2 molecule up to millihartree for the B atom.

The outstanding success of Hylleraas method calculations naturally led to attempts to extend the technique to systems with N > 2. The Hy method calculations we refer to have wave functions constructed using products of powers of r_{ij} such that

$$\Psi_{Hy} = \Psi(r_{ij}^\nu, r_{kl}^\mu, r_{mn}^\omega). \tag{7}$$

Note, here, the dependence of Ψ_{Hy} on powers of the interelectronic coordinate (including of course the linear one), not exponentials, and j can equal

k, i.e. there can be linked r_{ij} products. The incredibly accurate He atom calculations of Schwartz[20,21] and Nakatsuji and coworkers[22,50] employ what can be considered to be analytical wave functions which contain all kinds of terms which are important for the description of the correlation energy to this level of precision. These terms are not only powers of r_1, r_2, and r_{12}, but also logarithmic terms of r_1 and r_2, negative powers and fractional powers of r_1 and r_2, etc. The Iterative Complement Iteration (ICI) wave function of Nakatsuji et al. can be represented as

$$\Psi_{ICI} = \Psi(r_{ij}, e^{-r_{ij}}, \ln(r_i), r_i^{-n}, r_i^{p/q}). \tag{8}$$

The logarithmic terms describe the region of coalescence of two electrons and the nucleus described by Fock.[53] ICI wave functions produce energies to 40 digit precision for He and hence go far beyond anything even modern experiments can achieve. Analytical wave functions like this one have not been applied to N > 2 electron systems. However Nakatsuji and Nakashima[54] have recently developed a new theory (FC-CFT) to allow them to do variational calculations for N > 2. Applications to date have been to precisions of tens of microhartrees for Li and microhartree for Be.[54] In an interesting new development, they have now adopted the Hy-CI approach of one r_{ij} per term in their free complement s_{ij}–assisted r_{ij} theory[55] to enable them to do a calculation on C (N = 6) with a precision of about 0.342 millihartree, second only to the ECG result.[38]

The Schwartz and ICI wave functions contained both linear r_{ij} and exponentially correlated r_{ij}s, a pairing which was first suggested by Hirschfelder.[56] Correlated wave functions containing only the exponential correlation are the exponentially correlated Slater wave functions (ECS)

$$\Psi_{ECS} = \Psi(e^{-r_{ij}}, e^{-r_{kl}}, e^{-r_{mn}}). \tag{9}$$

As pointed out by Thakkar,[57] use of exponentially correlated wave functions dates back to Slater[58] and Hylleraas.[2] Exponentially correlated r_{12} was shown by Thakkar and Smith[59] to give very good results for helium-like ions even with rather compact wave functions. These wave functions lead to very high precision for two-electron systems which requires generation and optimization of nonlinear parameters (thousands in the Korobov[46] calculation listed in Table 2).

When correlated wave functions contain Hirschfelder's pairing and contain both linear and exponential r_{ij}s, the wave functions are E-Hy. These wave functions lead to even higher precision than ECS for two-electron

systems, producing 34 digit precision for He.[49] See Harris[60,61] and references therein for a detailed discussion of this line of development.

The extension of the Hy method leads to a very high precision when applied to N = 3 electron atomic systems, and indeed some of the best calculations for Li have been done with the Hy method by Drake and coworkers.[3–5] However, as pointed out by King,[62] the faster convergence for the calculation of the nonrelativistic energy with Hy is counterbalanced by two other features of the general approach. The first is that the Hylleraas technique has not been extended to systems with more than four electrons. Second, even for four-electron systems, there are significant unresolved integration problems when Hylleraas basis sets are used,[63] which make it impossible to carry out a calculation without adopting either the double-linked Hy-CI restriction of at most two odd power r_{ij} factors (for a calculation of this type, see Ref. 40) or the current Hy-CI restriction of one odd power r_{ij} factor per term (for a calculation of this type, see Ref. 64). We believe that these problems can be overcome by using the Hy-CI method codeveloped by one of us[13,65] and also independently by Woźnicki[66] as the superposition of correlated configurations (SCC).

The Hy-CI method[65] suffers from neither the unresolved integration problems of the Hy technique nor the inability of the ECG technique to represent the electron cusp. In the Hy-CI approach the wave function is expanded as a linear combination of terms each of which contains at most one linear r_{ij} factor

$$\Psi_{Hy-CI} = \Psi(r_{ij}). \qquad (10)$$

The basic idea is to combine the relative computational ease and orbital picture of CI with the better convergence obtained with r_{ij} explicitly in the wave function. The slow convergence of CI has been demonstrated by the He calculation presented in Table 1, where the best CI for the ground state of He is accurate to only 5 decimal places[12], whereas the best He calculation is accurate to 45 decimal places.[21] To some extent, this shows how important the details of the electron–electron cusp are, i.e., the details of the behavior of the wave function as the electron–electron separation approaches 0. Introducing r_{ij} in the wave function overcomes this problem and has the advantage over other correlated wave function techniques that the most cumbersome integrals that are needed for atomic systems with an arbitrary number of electrons are dealt with already at the four-electron level. Nevertheless, even though the explicit inclusion of interelectronic

distances in a CI wave function may greatly reduce (because of the adequate treatment of the electron–electron interaction) the length of the expansion required for high precision, it is fair to say that it is at the cost of greatly increased complexity in the computational procedures. In the next section we will review Hy-CI atomic and molecular calculations.

The convergence of the Hy-CI method can be accelerated by generalizing the single r_{ij} of Hy-CI per term to a form of the generic type $r_{ij}^{\nu} \times e^{-\omega r_{ij}}$, i.e., the correlation factor for each term can be r_{ij}, $e^{-\omega r_{ij}}$, or $r_{ij} \times e^{-\omega r_{ij}}$. This method is called the exponential Hy-CI method (E-Hy-CI); its wave function can be represented as

$$\Psi_{E-Hy-CI} = \Psi(r_{ij}^{\nu} \times e^{-\omega r_{ij}}). \tag{11}$$

The method was first proposed by Wang et al.[67] and developed and applied by us in a calculation on the ground state of the He atom obtaining a precision of 21 decimal digits,[45] which was the first E-Hy-CI calculation reported in the literature. Note that when the exponent of the exponential is zero, the wave function reduces to the Hy-CI wave function and when the power of r_{ij} is zero, the wave function reduces to the ECS wave function.
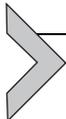
3. The Hy-CI methodology
3.1 One r_{ij} per term

Hylleraas-configuration interaction (Hy-CI) employs a novel wave function consisting of at most a single r_{ij} raised to the first power combined with a conventional nonorthogonal CI basis. We believe that this technique can be extended to multielectron systems, where the use of at most a single r_{ij} (to the first power) retains the power of r_{ij} factors in the wave function without making the integral evaluation overly complicated.

For high precision, the introduction of the interelectronic coordinate r_{ij} directly into the wave function has proven essential for few-electron systems. This is true for two,[6,12,20,46,68] three[69–73] and four–electron systems.[40,74,75] For two-electron systems, the best calculations[20–22] are special types that have not been extended beyond He.

As an example, consider beryllium. A Hy wave function for the ^{1}S ground state would be

$$\Psi = \sum_K C_K \Phi_K, \tag{12}$$

where the C_K are the variationally determined expansion coefficients. The basis functions Φ_K are of the form

$$\Phi_K = \widehat{O}_{as}\chi_K R_K, \tag{13}$$

where (for beryllium) $\widehat{O}_{as}$ is the four-electron antisymmetrizer and χ_K represents the spin function for term K. The radial functions R_K are what makes this Hy, and they are specifically of the form

$$\begin{aligned} R_K&(r_1, r_2, r_3, r_4, r_{12}, r_{13}, r_{14}, r_{23}, r_{24}, r_{34}) \\ &= r_1 r_2 r_3 r_4 r_{12} r_{13} r_{14} r_{23} r_{24} r_{34} e^{-\alpha_K r_1} e^{-\alpha_K r_2} e^{-\alpha_K r_3} e^{-\alpha_K r_4}. \end{aligned} \tag{14}$$

The problem is that there are already six products of r_{ij} in each term, in general. In practice, already at $N = 4$, calculations have been restricted to products of at most two r_{ij} factors per term, in what are called double-linked basis sets.[40] Interestingly, the work of the Kleindienst group[40,71,76,77] is called Hy-CI but starts out Hy, as the double-linked Be calculation demonstrates. However, Büsse mentions p orbitals in his thesis[78] and they are used by Merkens in a Be P state calculation.[77]

In contrast, in our Hy-CI method the wave function is expanded as a linear combination of terms Φ_K, each of which is a configuration (in the CI parlance) multiplied by at most one r_{ij} to some power. Specifically,

$$\Phi_K = \widehat{O}_{L^2}\widehat{O}_{as}\chi_K R_K, \tag{15}$$

where (for beryllium) $\widehat{O}_{as}$ is the four-electron antisymmetrizer and $\widehat{O}_{L^2}$ is an idempotent orbital angular momentum projection operator[79] projecting out the proper symmetry. R_K represents the spatial function for term K before antisymmetrization and projection, and is

$$R_K(r_1, r_2, r_3, r_4) = r_{ij}^{\nu_K} \prod_{s=1}^{4} \phi_{K_s}(r_s). \tag{16}$$

Here $\phi_{K_s}(r_s)$ denotes the sth basis orbital in the Kth term. The basis orbitals are taken by us to be unnormalized, nonorthogonal Slater-type orbitals (STOs)[13]

$$\phi(r, \theta, \varphi) = r^{n-1} e^{-\alpha r} Y_l^m(\theta, \varphi), \tag{17}$$

where the radial factor depends on the orbital exponent α and the radial quantum number n. The l and m quantum numbers define the order and degree of the orthonormal spherical harmonics Y_l^m.

R_K is a product of a "Hartree product" of orbitals (basically comprising a conventional CI configuration) multiplied by at most one r_{ij} factor.

When $\nu = 0$, the terms Φ_K of Eqs. (15) and (16) are what are referred to as configuration state functions (CSFs), where each CSF is an appropriate combination of Slater determinants, each of which has the spin and space symmetry of the state being computed.[80]

In contrast to Hy, in Hy-CI (with STOs) for atomic systems, the most cumbersome integrals that are needed for atoms with an arbitrary number of electrons are dealt with already in the four-electron problem (integrals are much less messy with just one r_{ij} per term). The restriction to at most one r_{ij} factor in a term, first proposed by James and Coolidge[81] in their calculations on the lithium atom, has to be lifted in Hy to get the highest precision wave functions. This may be the reason that the estimated demand on computer resources increases by a factor of about 6000 to reach spectroscopic precision for Li over He.[82] It just gets messier and messier. However in Hy-CI, we have shown[65] that the restriction to at most one r_{ij} factor in a term is reasonable. Important standard correlating factors, which are products of "unlinked" r_{ij} variables, can be represented by a single r_{ij} factor and excited orbitals of the STO basis (for example, $r_{12}2p(3)2p(4)$ can represent the correlation factor $r_{12}r_{34}^2$). Similar considerations apply for linked correlation factors like $r_{12}r_{24}^2$, i.e., products of r_{ij} are not needed in the expansion since important products of r_{ij} factors are handled by $r_{ij} \times p^2$, $r_{ij} \times d^2$, etc. This analysis neglects linked correlation factors where both r_{ij} powers are odd, as in $r_{12} \times r_{13}$. But these factors have been shown to be unimportant in a calculation on lithium.[69] We believe this is true in general, i.e., from an Hy perspective, the important products of r_{ij} factors are those that have a single r_{ij} to an odd power and can hence be represented easily in the Hy-CI method by a single r_{ij} factor times a CI configuration (or CSF). Since $r_{ij}^2 \approx p^2$, $r_{ij}^3 \approx r_{ij} \times p^2$, etc., only the odd powers of r_{ij} are needed and this properly focuses attention on the orbital basis. In our most recent work, starting with,[12] we restrict the r_{ij} further (to the first power). In summary, combining Hy and CI selects the more important term types in a variational expansion, simplifies the integral problem, and also makes treating states with angular momentum other than S more natural by incorporating the CI orbital picture into the method.

3.2 The integrals

The past 20 years have seen significant progress in the evaluation of Hy-CI integrals, following at least two distinctive paths. Ruiz starts from an expression for the Hamiltonian extracted from the eigenvalue problem of Hylleraas[2] by Pluvinage[83] and modified by Walsh and Borowitz[84] for more

complex systems. A detailed derivation of the Hamiltonian she uses can be found in Ref. 85. All expressions are derived fully using this Hamiltonian for atomic Hy-CI integrals in a series of papers.[86–88] The technique originated with Calais and Löwdin[89] and was used by Öhrn and Nordling in developing all of the Hy-CI integrals needed for extending Hy-CI to three-electron systems,[90] which involves integrating over the coordinates of one electron. Ruiz has also successfully used this method for the calculation of the requisite two- and three-electron kinetic energy integrals to high precision. The two-electron kinetic energy integrals are evaluated efficiently using a transformation which simplifies the problem, the Kolos and Roothaan transformation[91] which was used in the first Hy-CI calculations in 1971[13,65] and has been used by us ever since. For three-electron systems, Ruiz[92] transforms the kinetic energy part into the mutually independent distance coordinates r_i, r_{ij}, and the polar angles θ_i, and ϕ_i. This form of the Hamiltonian is appropriate for calculating integrals using Slater-type orbitals, not only for states of S symmetry but also for states with higher angular momentum.[93]

The method developed by Sims and Hagstrom[13] also goes back to the Öhrn and Nordling paper[90] which evaluated the integrals analytically by the use of auxiliary functions A and W (Larsson[69] used this technique in his very accurate, for the time, Li calculation). The 1971 paper[13] expands the treatment to four-electron integrals by introducing an X four-electron auxiliary function. Its revision over the last 20 years has been designed for efficient evaluation of all integrals and employs enhanced precision and parallel computing, which will be the focus of the next section. It is important to note that both integral evaluation techniques are used by us to check our programs, something that *cannot be emphasized enough*. For a detailed enumeration of all of the integrals arising in atomic Hy-CI and a discussion of the two different methods employed by us, see Harris.[94] The three-electron kinetic energy integrals can be efficiently evaluated by using a recent improvement of Harris.[95] All the integrals are analytical and have been checked by these different methods leading to the same quadruple precision results (approximately 30 decimal digits) to the precision reported in the various tables.[96,97]

3.3 Math and computational science issues

The fundamental premise of Hy-CI is that with the restriction to a single r_{ij} per term, all the integrals which have to be solved in the most general N-electron case are at most four electron integrals. In this section we first

take up how we have solved the mathematical issues that arise when using the Hy-CI technique when N > 2.[98–101] Then, since high CPU costs coming from the types of basis sets employed and the thousands of terms employed (which may require extended precision arithmetic) ultimately limit the routine use of such codes in a sequential environment, we discuss our use of MPI[102] to parallelize our code to hurdle this barrier.

It is our goal to demonstrate that this complexity can be overcome with a combination of the use of extended precision, parallel computing, and efficient techniques for integral calculation and storage. Hence, our first goal has been to identify and eliminate the real bottleneck to highly accurate Hy-CI calculations, the three-electron triangle integrals. Calculations based on exponentially correlated STOs only became practical (for N > 2 electrons) after the publication of an extraordinary paper by Fromm and Hill.[103] The same paper was used[98] to develop the formulas for evaluating these triangle Hy-CI integrals. In the first paper in the series,[99] the method is discussed in detail, as well as how to efficiently evaluate these integrals using recursive techniques at both the double precision and quadruple precision level of precision while trying to minimize the use of higher precision arithmetic. Also discussed is the use of series acceleration to overcome problems of slow convergence of certain integrals defined by infinite series. A direct + tail Levin u-transformation convergence acceleration[104] overcomes problems that arise when using other convergence acceleration techniques, and is the best method for overcoming the slow convergence of the triangle integral.

The math and computational science issues for the Hy-CI four-electron integrals were discussed in the papers II and III in the series.[100,101]

A parallel eigensolver proved essential for obtaining many of the atomic and molecular Hy-CI results discussed in this review. This involves solving the N-dimensional generalized eigenvalue problem

$$\mathbf{HC} = \lambda\mathbf{SC}, \tag{18}$$

by the inverse iteration method.[105] We solve this secular equation using our own portable parallel inverse iteration solver.[106] The generation of the matrices $\mathbf{H}$ and $\mathbf{S}$ is order N^2 while the solution of the secular Eq. (18) is order N^3. Since for us N is large and interprocessor communication is only order N^2, the parallelization of the H and S matrices is largely a matter of convenience (no restructuring of the code is required, just a suitable selection of columns by each process). We calculated the basic integrals on each process, taking up only a small fraction of the total time, but parallelized the

H and S matrix construction, allowing the total memory needed to be spread across the processors and eliminating the need to communicate matrix elements between processors. The result was that the whole process is almost "embarrassingly parallel" with near linear "speedup". All of this is discussed in our paper on the parallel GRSDEP (generalized real symmetric–definite eigenvalue problem) package, including how to obtain a quadruple precision FORTRAN 90+ version of the software.[106]

Even with greatly increased computational power and memory, and advances in efficient calculation of difficult integrals, the choice of basis set is crucial (and perhaps always will be). This is where "intuition" and/or experience comes into play. To put it another way, in calculating nonrelativistic energies, one chooses a suitable basis in terms of which the electronic wave function is parameterized. We believe that one has to introduce interelectronic coordinates to get high precision results. But the key insight is that a CI wave function is exact, with an infinite number of terms. The most natural way to overcome the problem of slow convergence is to introduce a single interelectronic coordinate, giving in principle an exact solution, and then letting the variational method bring in the r_{ij} effect where needed. With only a single r_{ij} in any term, the most difficult integrals are four-electron integrals, arising in Be. If the Hy-CI idea is a good one, then a Be calculation will show conclusively whether high–precision calculations can indeed be done for atoms with $N \geq 4$ using the Hy-CI technique.

4. The Hy-CI atomic calculations

This section reviews nonrelativistic Hy-CI calculations on atoms from $Z = 2$ through 5 (He through B). For information on the extension of Hy-CI to the relativistic domain by Pestka, see Refs. 107, 108.

4.1 He atom

For the He atom, there is only one interelectronic coordinate, namely r_{12}, which makes Hy, Hy-CI, and CI-R12 (using STOs and evaluating all integrals analytically rather than numerically) essentially equivalent. Sims and Hagstrom compared Hy, CI, and Hy-CI in their 2002 He calculation[12] and Ruiz included CI-R12 in her study.[24] Our interest here is strictly on Hy-CI (and E-Hy-CI): not just the wave functions and energies computed variationally with them but also ultimately in the computation of atomic properties which the wave functions enable. For example, Hy-CI has been used by Bylicki[109,110] and Bylicki and Nicolaides[111] to compute atomic

resonances, and it has been used by Bylicki and Bednarz[68] to compute the most precise energy for the $2p^2$ $^3P^e$ state of the H^- ion. In 2010 Ruiz coauthored a paper[112] which used Hy-CI to compute nonrelativistic energies for the ground and ten excited S states of the lithium ion, some of which represented the highest level of precision ever reached in atomic quantum computations for these states, hence demonstrating that the Hy-CI technique is effective for not only the ground state of small atomic systems but also for excited (including highly excited) states. The 10th excited S state computed is actually the 25th excited state (since states of different symmetry interleave the computed S states). With these results and a He ground state Hy-CI wave function of the type later reported in Ref. 24, Frolov and Ruiz were able to determine transition probabilities to the various final states of the β^- decaying He atom. This work represents one of the first applications of highly accurate atomic physics methods to nuclear physics. Various β^- decaying nuclei are of interest in nuclear medicine and having a mechanism for predicting the probability of formation of various final (or post–decay) atomic states with a high degree of precision is of significant interest to researchers in the field.

The best Hy-CI calculation is actually that in our 2020 study of the ^1S ground state of the He atom with E-Hy-CI.[45] The Hy-CI calculation reported there took the 2002 study higher in l, going from $l = 7$ to $l = 10$, and in the process only changed the calculated energy by one decimal digit, from 19 decimal digits to 20 decimal digits. A detailed breakdown of this result is displayed in Table 3. Note that convergence is fast early in the calculation, whereas after $l \geq 5$, it is slower. Precisely this ultimately slow convergence of Hy-CI will hopefully speed up for an E-Hy-CI wave function. This is the case for the ^1S ground state of the He atom.[45]

4.2 Li atom

Now that the Hylleraas (Hy or Hy-r_{ij}) method has been extended so that it is possible to calculate *essentially exact for all practical purposes* nonrelativistic energies for He and other three body systems, the Li atom has become the next testbed. With three electrons, its ground state configuration $1s^2 2s$ is a doublet S state with an unpaired electron in the valence shell, a situation similar to the H atom.

The first Hy-CI calculations were the ones of Sims and Hagstrom[113] who computed the four lowest ^2S and the four lowest ^2P states to a tenth of a millihartree, state of the art at that time. They computed rigorous upper

Table 3 Hy-CI calculation of the ^1S ground state of the He atom.[45]

N	l	n	E (hartree)
760	0	19	**–2.903**4 9832 0585 8801 1976 9235
1520	1	19	**–2.9037 24**26 8354 6045 9864 6392
2280	2	19	**–2.9037 2437** 6954 6918 8919 8809
2964	3	18	**–2.9037 2437 7034** 0541 4170 4466
3444	4	15	**–2.9037 2437 7034 1195** 3899 2122
3864	5	14	**–2.9037 2437 7034 1195 98**22 0159
4284	6	14	**–2.9037 2437 7034 1195 98**29 6249
4648	7	13	**–2.9037 2437 7034 1195 98**29 9927
6160	10	9	**–2.9037 2437 7034 1195 9831** 0465
Exact[20–22]			**–2.9037 2437 7034 1195 9831 1159**

N is the number of terms, l is the maximum angular momentum, and n is the maximum principal quantum number employed for this l-wave.

and lower bounds for 16 lines arising from allowed transitions among these four ^2S and four ^2P states with the bounds estimated to be 3.5%,[114] as well as electric polarizabilities by a lower bound procedure.[115] Photo–absorption and ionization cross sections in atomic lithium were also investigated using a Stieltjes–Tchebycheff procedure.[116,117]

The next Hy-CI calculations on Li were those of Pipin and Bishop[70] and Pestka and Woźnicki[118] who achieved microhartree precision. The most accurate Hy-CI calculation on the Li atom is by Sims and Hagstrom[42] in 2009, which addressed whether linked products[d] like $r_{12}^m r_{13}^n$, *with odd–odd powers* are necessary in Hy. This is important since it is the odd–odd r_{mn} products that lead to some very difficult integrals and which are presumably the reason there are no really accurate Hy calculations for atoms with more than three electrons. Pipin and Bishop[70] were able to achieve microhartree precision in an Hy-CI calculation on lithium, showing that such terms are unimportant at the microhartree level of precision. Since odd–odd linked products are by definition excluded in Hy-CI, the precision obtainable in Hy-CI without them is also an issue. In their 2009 calculation, Sims and Hagstrom were able to achieve sub-nanohartree precision for the Li ground

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[d] By linked products we mean r_{mn} products with a common index, like $r_{ij}^m r_{ik}^n$. Unlinked terms (like $r_{ij}^m r_{kl}^n$, no common index) do not occur in Li.

state using Hy-CI without such terms, and were able to further show that with the Hy method, these factors are only important at the sub–nanohartree level of precision! They also showed how to pick expansion terms in an Hy-CI calculation both from CI considerations and by using the expansion of likely Hy r_{ij} products as a guide. We believe that in general, from an Hy perspective, the important *linked* products of r_{ij} factors are those that have a single r_{ij} factor to an odd power which can then easily be represented in the Hy-CI method by a single r_{ij} factor times appropriate CI terms (CSFs). For example,

$$
\begin{aligned}
sssr_{12}r_{13} &= (ss + pp + dd + ff)sr_{13}, \\
sssr_{12}r_{23} &= (ss + pp + dd + ff)sr_{23}, \\
sssr_{13}r_{23} &= s(ss + pp + dd + ff)r_{13},
\end{aligned}
\tag{19}
$$

where the equals sign means is represented by and the plus signs stand for linear combinations of. From Table 4 it can be seen that an *sp* r_{ij} basis is in error by only about 1 microhartree, 3 nanohartree precision is achievable with an *spd* r_{ij} basis, and sub-nanohartree with an *spdf* r_{ij} basis. Not only was the ground state energy calculated in this study but also the first 5 excited states of ^2S. The results for the $4\,^2S \Rightarrow 7\,^2S$ improved substantially on previous work, demonstrating that the conclusions drawn for the ground state also apply to excited states (at least for *S* states).

A truncated version of the Sims and Hagstrom wave function expansion is shown in Table 4. Terms are shown by orbital type and R means all configurations with orbitals of that type from the basis set and 1, r_{12}, r_{13}, and r_{23}.

Table 4 Hy-CI calculation on the ^2S ground state of the Li atom.[42]

Terms added	N	E (hartree)[42]	ΔE (nh)
sss R	2916	**-7.47**7 634 670 861	
pps R	4708	**-7.478** 059 148 015	–424477.2
dds R	5572	**-7.478** 059 958 638	–810.6
psp, spp R	8316	**-7.478** 060 224 321	–265.7
dsd, sdd, ppd, pdp, dpp, ddd R	13500	**-7.478 060 32**0 454	–96.1
fpd, pfd, fdp, pdf, dfp, dpf, ffs, sss R	16764	**-7.478 060 323** 451 9	–3.0
Estimated exact (Hy)[7]		**-7.478 060 323 910** 147(1)	
Estimated exact (ECS)[51]		**-7.478 060 323 910** 2(2)	

In the table R={1,r_{12},r_{13},r_{23}}, N is the number of terms added, and only orbital types x R are shown.

While these calculations are computationally expensive, they can be used as a guide to constructing more compact wave functions. For example, Ruiz et al. have calculated the nonrelativistic energies of about 40 bound S, P, D, F, G, H, and I states in the three-electron Li atom and Be^+ ion, respectively, using about 700 terms.[119,120] For the ground and low-lying excited states, their best precision was 1×10^{-6} hartree and 1×10^{-4} hartree for the other states. All of the calculated energies properly interleave (the order of the states S < P < D < F < G < H < I < K < L < M < N … agrees with the experimental spectra), demonstrating the utility of the Hy–CI wave function not only for S states but also for the calculation of states with non-zero angular momentum, and for cations as well as neutral atoms. These Hy–CI wave functions for the Li atom and Be^+ ion enabled the determination of transition probabilities to the various final states of the β^- decaying Li atom.[121]

The Li atom calculations have demonstrated the unimportance of linked odd–odd products of r_{ij}; the Be atom will test how important unlinked products like $r_{12}r_{34}$ will turn out to be for systems with more than three electrons.

4.3 Be atom

Beryllium, with its four electrons and strong mixing of the $1s^2 2s^2$ and $1s^2 2p^2$ configurations, has long been a testbed of theories. Bunge did his first Be calculation in 1968[122] and his CI calculations for Be improved steadily, culminating in a benchmark calculation of over 2.6 million terms in 2010.[30] While significant progress was being made in Hy treatments of three-electron systems, integral problems with the conventional Hy expansions[63,123,124] brought calculations to a halt for four-electron systems until finally, in 1998, Büsse et al.[40] made major improvements through the use of Hy-type doubly linked terms in the wave function expansions. This was the first major Hy-type calculation of near microhartree precision. In 1995 the exponentially correlated Gaussian (ECG) method was introduced by Komasa et al.[75] The relative simplicity of the resultant integrals led to impressively accurate calculations, culminating in the work of Adamowitz and coworkers[125,126] which stands as the best to date.

One of the coauthors has been contributing to this discussion since 1971, when he coauthored the first Hy-CI calculation on the ^1S ground state of the Be atom and in the process introduced the Hy-CI method.[13,65] The millihartree precision achieved using about 100 terms represented state of the art at the time. That was followed by the calculation of the $1s^2 2s^2\ ^1S$

and $1s^2 2s2p\ ^1P$ states of Be I, C III, and O V,[127] which led to the calculation of transition probabilities, including upper and lower bounds, for the lowest $^1S \rightarrow {}^1P$ transition. Interpolative techniques were used to make a graphical study of the transition probability behavior along the isoelectronic sequence, resulting in transition probabilities for the isoelectronic sequence with rigorous upper and lower bounds of (7–10)% and probable precision of $\leq 2\%$. Interestingly, all of the experimental data fell outside the bounds. About nine months after publication of the paper, a new experiment was done obtaining perfect agreement with the Hy-CI computed value, demonstrating the predictive power of Hy-CI. Not only were transition probabilities computed but electric polarizabilities with a lower bound as well.[128] In 2011 they returned to the ^1S ground state using a much larger basis, a parallel program and higher precision, and improved the precision to a tenth of a microhartree.[129] A condensed version of that calculation is given in Table 5, where the digits which are correct are highlighted in each line.

The Be atom in its ground configuration of $1s^2 2s^2$ has two shells doubly occupied (with, as mentioned, strong mixing of the $1s^2 2p^2$ configuration). The ability of Hy-CI calculations to achieve $0.1\mu h$ precision for beryllium is shown, which demonstrates again the unimportance of linked odd–odd

Table 5 Hy-CI calculation on the ^1S ground state of the Be atom.[129]

Terms added	N	E (hartree)[129]	ΔE (μh)
ssss R	4480	**-14.66**29 3492 2212	
ppss, sspp, spsp, spps R	16835	**-14.6673** 1661 8713	-4381.7
pppp R	20330	**-14.6673 5**033 6946	-33.7
sppd, ppsd, sdpp, pspd, dpsp, pdsp R	31793	**-14.6673 5**419 4814	-3.9
ssdd, ddss, sdds R	36715	**-14.6673 5**614 6219	-2.0
ddpp, ppdd R	39887	**-14.6673 56**32 4785	-0.2
ssff, ffss, sffs R	40974	**-14.6673 56**37 8257	-0.1
ssss R	41871	**-14.6673 56**41 1043	-0.03
Hy[40]	5306	**-14.6673 5**47	
Lowest upper bound (ECG)[16]	7000	**-14.6673 56**50 7	
Estimated exact[16]		**-14.6673 56**50 8(1)	
Estimated exact[52]		**-14.6673 6**	

In the table R={1,r_{12}, r_{13}, r_{14}, r_{23}, r_{24}, r_{34}}, N is the number of terms added, and only orbital types are shown.

products of r_{ij}. There are a few important blocks incorporating intershell correlation (r_{13} and r_{14} terms being the most important). The unlinked $r_{ij}r_{kl}$ (no indices in common) term types, which first occur in the four-electron case, are represented with one-electron pair correlated primarily by the r_{ij} factor while the other pair is correlated by a CI pair expansion, specifically, $(ss + pp + dd + \cdots)_K (ss + pp + dd + \cdots)_L r_{34} + (ss + pp + dd + \cdots)_K r_{12}$ $(ss + pp + dd + \cdots)_L$, where K and L refer to the K and L shells, respectively.

The convergence of $r_{12}r_{34}$ term types was investigated, and Hy–CI accurately represented this term type at the tenth of a microhartree level. Given the close relationship between Hy–CI and Hy calculations when the Hy expansion terms contain at most a single odd power of r_{ij}, the results suggest that it should be possible using Hy expansions to achieve comparable precision for beryllium without using the odd–odd power products of r_{ij}, which lead to severe integral problems in Hy calculations for four or more electrons.

This work was continued in 2014 with enhanced calculations on the entire Be isoelectronic sequence from Z (nuclear charge) = 4 all the way through 113.[43] With this wave function, 10 nanohartree results were easily obtained, and so a few members of the isoelectronic sequence for which there were good reference results for comparison were tried next. Again 10 nanohartree results were obtained, using a simple scaling of the orbital exponents by Z/4 (the ratio of nuclear charges since Z = 4 for Be), and by using these rather ambitious variational calculations combined with a fitting polynomial, 10 nanohartree or better precision was obtained for the entire beryllium ground state isoelectronic sequence. Li$^-$ (with Z = 3), nominally the first member of this series, has a decidedly different electronic structure than the rest of the isoelectronic sequence and was not included in those calculations and subsequent discussions. The Hy–CI Li$^-$ calculation was carried out in 2017[130] with similar results.

To test how well the convergence of the $r_{12}r_{34}$ term type ("double cusp problem") is treated in Hy–CI, the calculations presented in Table 6 were done. Compared to the slow, cusp-connected convergence in typical CI calculations, this is fast convergence, suggesting that this correlation type can be accurately, albeit slowly, represented within the Hy–CI model. Modifying the Hy–CI model to include unlinked $r_{ij}r_{kl}$ products (no indices in common, a "double-unlinked Hy–CI") is an avenue for future research. Another possibility would be to consider using E-Hy–CI in the hope that the exponential r_{ij} would speed up the convergence, as it did in Ref. 45.

Table 6 Convergence of $r_{12}r_{34}$ as represented by Hy-CI.

Terms added	N	N_{tot}	$E(N_{tot})$ (hartree)	ΔE (µh)
$s_K s_K s_L s_L$	896	896	−14.5916 8499 6456	
$p_{Kp}\, p_{Kp}\, s_L s_L$	539	1435	−14.6297 7998 1630	−38094.985175
$s_K s_K\, p_{Lp}\, p_{Lp}$	539	1974	−14.6589 6443 5905	−29184.454275
$p_{Kp} p_{Kp} p_{Lp} p_{Lp}$	658	2632	−14.6610 8625 6532	−2121.820627
$s_K s_K s_L s_L r_{12}$	896	3528	−14.6665 2350 2244	−5437.245712
$s_K s_K\, p_{Lp}\, p_{Lp}\, r_{12}$	539	4067	−14.6669 3690 3188	−413.400944
$s_K s_K\, d_{Ld}\, d_{Ld}\, r_{12}$	345	4412	−14.6669 5344 8529	−16.545342
$s_K s_K\, f_{Lf} f_{Lf} r_{12}$	198	4610	−14.6669 5615 7867	−2.709337
$s_K s_K\, g_{Lg}\, g_{Lg}\, r_{12}$	97	4707	−14.6669 5729 2953	−1.135086
$s_K s_K s_L s_L r_{34}$	896	5603	−14.6669 6704 8825	−9.755872
$p_{Kp}\, p_{Kp}\, s_L s_L r_{34}$	539	6142	−14.6669 6756 8180	−0.519356
$d_{Kd}\, d_{Kd}\, s_L s_L r_{34}$	312	6454	−14.6669 7305 3737	−5.485557
$f_{Kf} f_{Kf}\, s_L s_L r_{34}$	185	6639	−14.6669 7405 1162	−0.997425
$g_{Kg}\, g_{Kg}\, s_L s_L r_{34}$	94	6733	−14.6669 7410 8532	−0.057369

N is the number of terms added and N_{tot} is the cumulative number of terms.

Hy-CI has from its inception been an attempt to extend the success of the Hy method to systems with more than three electrons. For both extension of the method to $N > 4$ as well as for excited states of four-electron systems, how well the method handles the "problem double cusp" when the L shell is more diffuse than in the ground state needed to be studied, which was the purpose of a subsequent study[131] which examined successively higher states of Be of ^1S symmetry. Specifically, a study of the Be(2sns) excited states, n = {3,7} was carried out. Based on the calculations reported in Ref. 131, one can conclude that this correlation type can be accurately represented for the more diffuse distribution of Be excited states of ^1S up through 7 ^1S. Combined with the previous Be isoelectronic series results, these calculations exemplify the level of precision that is now possible with Hy-CI in describing not only the ground state of Be and Be-like ions but also excited states (S and non-S, singlet and triplet) as well as Be-like ions and the anion.

4.4 B atom

The Boron atom with its five electrons is the first atom whose ground state is not an S state, being a doublet state of P symmetry (^{2}P). Its ground configuration $1s^2 2s^2 2p$ is strongly mixed with $1s^2 2p^2 2p$ due to the quasi-degeneracy of the 2s and 2p orbitals, mimicking the situation in the Be atom. For Hy-CI the integrals required have already been treated at the N = 4 level, but the complexity of the calculation increases as the size increases (there are more integrals and much bigger matrices are needed to maintain precision) and there are potential linear dependency problems (see linear dependence in Hy-CI calculations of the He atom).[132]

Ruiz[44] developed the first Hy-CI computer program for the B atom in Fortran 90 with quadruple precision (about 30 decimal digits of precision). Her program was structured both to take advantage of the idempotency of the Hamiltonian, antisymmetrization, and spin and orbital momentum operators[79] to make the program as efficient as possible, and to be general enough to investigate systems with N > 5. Table 7 summarizes the calculations Ruiz[44] performed on the ground ^{2}P state of boron atom using an *spd* STO basis set. One can see the effect on the energy of adding configurations

Table 7 Hy-CI calculations on the ^{2}P ground state of the B atom.

Terms added	N	N_{tot}	E (hartree)	ΔE (μh)
ssssp, sssps, spsss	406	406	**–24.5**556 4742	
ssppp, ppssp, sppsp	249	655	**–24.6**167 9454	–61147.12
ppppp	2	657	**–24.6**177 2748	–932.94
ssspd, sssdp, sspds, pdsss, spsds, sdssp	242	899	**–24.6**390 3370	–21306.22
ssddp, sspdd, sdsdp	32	931	**–24.6**414 2490	–2391.20
sppdp, spppd, ppsdp, ppspd	13	944	**–24.6**417 8394	–359.04
pppdd, ddppp, ppddp	7	951	**–24.6**418 8635	–102.41
ddddp	3	954	**–24.6**418 8666	–0.31
ssssp × r_{12}	1	955	**–24.6**464 6510	–4578.44
ssssp × r_{13}	1	956	**–24.6**467 5150	–286.40
ssssp × r_{15}	1	957	**–24.6**467 5158	–0.08
ssssp × r_{34}	1	958	**–24.6**474 4083	–649.25
ssssp × r_{35}	1	959	**–24.6**474 4415	–3.32

Table 7 Hy-CI calculations on the ^{2}P ground state of the B atom.—cont'd

Terms added	N	N_{tot}	E (hartree)	ΔE (µh)
$ssssp \times R$	199	1158	–**24.6**481 4522	–701.07
FCI[31]		7 million	–**24.6538** 00034	
ECG[37]		8192	–**24.6538** 67537	
Estimated[37]			–**24.6538** 6805 (45)	
Estimated exact[52]			–**24.6539** 1	

In the table $R = \{1, r_{12}, r_{13}, r_{14}, r_{15}, r_{23}, r_{24}, r_{25}, r_{34}, r_{35}, r_{45}\}$, N is the number of terms added of a particular orbital type, N_{tot} is total number of terms added, and only orbital types are shown.

containing r_{ij} terms. As expected, correlated configurations of s-type pick up the most correlation energy. The r_{12} and r_{34} configurations illustrate the importance of the $r_{12}r_{34}$ double cusp for systems with N > 4, and the r_{13}, r_{15} contributions show that K–L intershell correlation between s orbitals is more important than intershell correlations between s and the L shell p orbital. Further investigations, including investigating the effect of adding f and perhaps higher angular momentum orbitals, will be required to achieve an Hy–CI precision for B approaching that of Be, which would make it competitive with the results achieved by other methods (see Table 7).

5. E-Hy-CI atomic calculations

We have seen how CI has been enriched by the explicit inclusion of r_{ij}, which gives the exact wave function at the coalescence point as r_{ij} goes to 0. It was recognized long ago that the exact wave function should also vanish at infinity. It was Hirschfelder in 1963[56] who suggested that $e^{-\omega r_{ij}}$, ω positive, has the correct asymptotic behavior as r_{ij} goes to infinity, and suggested that it be paired with a linear r_{ij} term, but he did no calculations. Since then, exponential correlation factors, with or without the linear terms, have been included in calculations by several authors, as we have seen in the discussion of ECS and E-Hy in Section 2. Also mentioned there is the E-Hy-CI method proposed in 2012 by Wang et al.,[67] who developed the integrals but did no calculations. That situation was remedied when we undertook a systematic study aimed at a comparison of the performance of E-Hy-CI vs Hy-CI.[45]

This study was undertaken to find out whether the ultimately slow convergence of Hy-CI (arising from the $r_{12}r_{34}$ double cusp as we have seen) can

be speeded up by pairing exponential and linear correlation factors in an E–Hy–CI wave function, defined in Eq. (11). For details, see Ref. 45. The Hy–CI restriction to one r_{ij} per term becomes in E–Hy–CI one pairing of exponential and linear r_{ij} per term. When the power of the linear term is zero, E–Hy–CI reduces to an ECS wave function, whereas making the exponent zero gives an Hy–CI wave function. If both are zero, the wave function becomes a CI wave function. Therefore the E–Hy–CI wave function can be considered a generalization of the ECS, Hy–CI and CI wave functions.

To see why we undertook the E–Hy–CI study, consider the Hy–CI calculations on the He atom of Table 3, a slightly bigger calculation than the one performed by Sims and Hagstrom[12] with 20–digit precision. It can be seen that the precision increases rapidly when adding successively p, d, and f orbitals, but as the precision increases, the convergence slows down, a situation one hopes E–Hy–CI can alleviate.

Our calculations are the first E–Hy–CI calculations to appear in print. The new E–Hy–CI kinetic energy integrals that were needed (the ones including the exponentially correlated terms) were derived by Padhy.[133,134] As the starting point for the calculations we took our Hy–CI calculations[12,24] and added the exponential term $e^{-\omega_{12}r_{12}}$. The calculations were done in quadruple–double with exponent (QDE) precision, twice quadruple precision and producing > 60 decimal digits. By comparing convergence of the E–Hy–CI wave function expansion to that of the Hy–CI wave function without exponential factors, both convergence acceleration and an improvement in the precision for the same basis were demonstrated. While ultimately the E–Hy–CI convergence resembles that of Hy–CI,[e] 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,[f] very promising. A condensed version of the results is presented in Table 8.

Table 9 compares the E–Hy–CI results with other calculations of the ^{1}S ground state. The first is the Frankowski and Pekeris[135] calculation using

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[e] The $l = 6$ E–Hy–CI result is however superior to the $l = 10$ result for Hy–CI.[45]
[f] Hy–CI and its extension to E–Hy–CI are unique in this regard.

Table 8 Comparison of Hy-CI and E-Hy-CI.

Method	l	n	α	ω_{12}	N	E (hartree)
Hy-CI[a][24]	0	20		2.9814	420	**–2.903**4 9813 3768 2647 9878
E-Hy-CI[45]	0	20	0.5	2.9814	840	**–2.9037 243**5 3896 0173 3543
Hy-CI[a][24]	1	19		2.9814	800	**–2.9037 24**26 7864 5688 1088
E-Hy-CI[45]	1	19	0.5	2.9814	1600	**–2.9037 2437 703**3 2396 1091
Hy-CI[a][24]	2	18		2.9814	1142	**–2.9037 2437** 6943 7414 6155
E-Hy-CI[45]	2	18	0.5	2.9814	2284	**–2.9037 2437 703**3 6475 6471
Hy-CI[a][24]	3	17		2.9814	1452	**–2.9037 2437 70**24 3236 8211
E-Hy-CI[45]	3	17	0.5	2.9814	2896	**–2.9037 2437 703**3 8188 1906
Reference[20–22]						**–2.9037 2437 7034 1195 9831**

[a]Calculation from Ref. 24 repeated in QDE precision arithmetic.
N is the number of terms, l is the maximum angular momentum quantum number, and n is the maximum principal quantum number employed.

Table 9 Summary of the best calculations on the ^{1}S ground state of the He atom.

Technique	N	E (hartree)
Analytical[135]	246	**–2.9037 2437 7032** 6
Analytical[136]	230	**–2.9037 2437 7034** 0
ECS[137]	308	**–2.9037 2437 7034 11**44
Hy[4]	1262	**–2.9037 2437 7034 119**4 8
ECS[138]	2200	**–2.9037 2437 7034 1195 98**29 6
Hy[6]	2358	**–2.9037 2437 7034 1195 983**0 5
Hy-CI[45]	6160	**–2.9037 2437 7034 1195 9831** 0465
E-Hy-CI[45]	10080	**–2.9037 2437 7034 1195 9831 1**084
ECS[46]	5200	**–2.9037 2437 7034 1195 9831 115**8
E-Hy[49]	22000	**–2.9037 2437 7034 1195 9831 1159 2451 9440 44**3
ICI[22]		**–2.9037 2437 7034 1195 9831 1159 2451 9440 4446 6969** 0537
Analytical[20,21]	10259	**–2.9037 2437 7034 1195 9831 1159 2451 9440 4446 6969 253**0 9838
Extrapolated[21]		**... 6969 253**1 05

N is the number of terms.

perimetric coordinates, a remarkable result for the year it was accomplished (1966). This was later improved to picohartree precision by Freund, Huxtable, and Morgan.[136] The Thakkar and Koga[137] ECS calculation was very compact and accurate. The Drake and Yan[4] Hy calculation in 1994 was improved some years later by Drake, Cassar, and Nistor.[6] The Korobov ECS calculation[138] which optimized exponents for the different regions was improved several years later[46] and is one of the best and most compact calculations on the He atom. Our results[45] are very close to the ones of Korobov using ECS with exhaustive optimization of the nonlinear parameters. The Hy-CI and E-Hy-CI calculations are surpassed only by the most accurate ones, those of Korobov,[46,49] Nakatsuji et al.,[22] and Schwartz,[20,21] the last of which is an amazing 45 decimal digit precision.
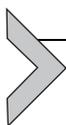
6. Hy-CI molecular calculations

The first Hy-CI calculations for systems other than atoms were carried out by Clary[139,140] and Clary and Handy.[141,142] Clary and coworkers used STOs in demonstrating the utility of the technique for one-positron atomic systems and for many-electron diatomic molecules. Clementi's group[143–145] successfully used GTOs in Hy-CI for diatomic molecules. For a complete review of this branch of Hy-CI, see the review article by Rychlewski.[146] Preiskorn and Woźnicki[147,148] were the first to use GTOs for the basis functions in Hy-CI calculations instead of STOs.

6.1 High-precision calculation of the H_2 bond dissociation energy

On the diatomic molecular side, the presence of two fixed nuclei rules out exact analytical solutions to the molecular nonrelativistic Schrödinger equation (in the Born-Oppenheimer (BO) approximation) except for the one-electron H_2^+ ion and other equivalent one-electron systems. Dihydrogen, H_2, has the distinction of being the first molecule whose dissociation energy was correctly predicted by quantum mechanical calculation (1968) before this same quantity was measured reliably by experiment. Today we may again be witnessing a situation in which quantum mechanical calculations yield more accurate determinations of this fundamental property than can be measured experimentally.

Very high-precision approximations are now available for molecular hydrogen (a two-electron system), see Table 10. Sims and Hagstrom calculated[41] Born-Oppenheimer (BO) energies for 47 internuclear distances in

Table 10 Calculations on the Born-Oppenheimer energy of the ground state of the H_2 molecule at internuclear distance 1.4 bohr and equilibrium bond distance 1.4011 bohr.

Technique	N	R	E (hartree)
ICI[50]		1.4	**–1.174 475 714** 138
Hy–CI[41]	7034	1.4	**–1.174 475 714 220** 075 5
ECG[35]		1.4	**–1.174 475 714 220** 363
Estimated[39]		1.4	**–1.174 475 714 220** 443 4(5)
ICI[50]		1.4011	**–1.174 475 931 39**7 74
Hy–CI[41]	7034	1.4011	**–1.174 475 931 399** 84
ECG[35]		1.4011	**–1.174 475 931 400** 135
Hy[39]	22,363	1.4011	**–1.174 475 931 400** 215 99
Estimated[39]		1.4011	**–1.174 475 931 400** 216 7(3)

the range of 0.4 bohr to 6.0 bohr with > 12 digit precision. Their nonrelativistic energy is –1.1744 7593 1399(1) hartree at the bond equilibrium $R = 1.4011$ bohr distance. The BO energies provided the $^1\sum_g^+$ potential energy curve which was critical to determining, theoretically, the dissociation energy D_0 of H_2. These results were, when calculated, the most accurate energy values ever obtained for a molecule of that size, 100 times better than the best previous calculated value or the best previous experimental value. Piszczatowski et al.[149] obtained a new theoretical bond dissociation for the hydrogen molecule by fitting the Born-Oppenheimer potential needed in the computation to the energies computed by Sims and Hagstrom over 47 internuclear distances ranging from 0.4 to 6.0 bohr. The bond dissociation energy so obtained, 36118.0693(10) cm^{-1}, was precise to 9 significant digits, two orders of magnitude better than the best previous experimental result.

6.2 Mathematical techniques for molecular calculations

One of the techniques used to expand the use of explicitly correlated wave functions to the highly precise calculation of molecular or many–center states is to use the nonrelativistic Hamiltonian for n–electron and N–nuclear center molecules in Hylleraas coordinates.[150] The kinetic energy part is transformed into the interparticle distance coordinates $r_{i\mu}$, r_{ij}, and internal polar angles $\theta_{i\mu}$, and $\phi_{i\mu}$ of the electrons with respect to every nucleus. This form of the

Hamiltonian is appropriate for obtaining the matrix elements in molecular calculations using wave functions with Slater or radial Gaussian orbitals.

Slater-type orbitals are the natural basis functions in multicenter quantum molecular calculations, but they lead to complicated multicenter integrals which have restricted their use. While in practice the pragmatic solution has been to expand the STOs in a linear combination of GTOs (to make the integrals easier),[151] research on the integral problems has continued in hopes of alleviating the extremely long computational times, slow convergence and inaccuracies in the calculation of properties that their use entails. A book[152] devoted to advances in molecular integrals over Slater orbitals has been edited by Ruiz; the book includes two-center integrals over STOs with a correlation factor and even discusses relativistic Hy-CI. Another review[153] coauthored by Ruiz discusses how both the long range behavior and the cusp conditions when two particles approach each other make STOs the natural basis functions (molecular orbitals) for quantum molecular calculations, and how there has been a renewed interest in their use as basis functions for both molecular CI and Hy-CI calculations. Included in the review is a chapter on explicitly correlated methods for molecules which the interested reader is referred to.

While the power of molecular Hy-CI in molecular calculations has been demonstrated in the H_2 calculation we have discussed above, it is fair to say that the application of Hy-CI to molecular problems is in its infancy. Given the incredible amount of CPU power that can be brought to bear on molecular problems nowadays, the future looks bright for molecular Hy-CI.

6.3 Summary

For N > 1, no exact analytical solutions of Schrödinger's equation are known. The wave functions of many-electron atoms are highly complex. The essential problem is the conflict between the electron–electron repulsion term, which couples electrons together in an intricate dance of mutual avoidance, and the electron-nuclear attraction, which concentrates electrons into regions of space nearest to the nucleus. An electron "wants" to be close to the nucleus and far away from the other electrons at the same time, introducing extraordinary complexity into the wave function.

Variational methods based on explicitly correlated methods 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 much so that a book dealing entirely with explicitly correlated functions has relatively recently been produced.[25] Of the correlated methods, Hy has problems at the $N = 4$ level, leaving only ECG and Hy-CI for $N \geq 4$. Now that Be is being done by both methods at better than 10 nanohartree precision, the next frontier is B ($N = 5$), where the best calculation is ECG and took a year on 24 processors to achieve only 2 micro–hartree precision. How well Hy-CI can do remains to be seen.

Acknowledgments

References

1. Clementi, E.; Corongiu, G. From Atoms to Large Chemical Systems With Computational Chemistry. *Rev. Inst. Fr. Pétrol.* **1996**, *51* (1), 19–35.
2. Hylleraas, E. A. Neue Berechnung der Energie des Heliums im Grundzustande, sowie des tiefsten Terms von Ortho-Helium. *Zeit. Phys.* **1929**, *54*, 347–366. https://doi.org/10.1007/8F01375457.
3. Drake, G. W. F. High-Precision Calculations for the Rydberg States of Helium. In *Long-Range Casimir Forces: Theory and Recent Experiments on Atomic Systems*; Levin, F. S., Micha, D. A., Eds.; Plenum: New York, 1993; pp. 107–217.
4. Drake, G. W. F.; Yan, Z. C. Variational Eigenvalues for the S States of Helium. *Chem. Phys. Lett.* **1994**, *229*, 486–490.
5. Yan, Z. C.; Tambasco, M.; Drake, G. W. F. Energies and Oscillator Strengths for Lithiumlike Ions. *Phys. Rev. A* **1998**, *57* (3), 1652–1661.
6. Drake, G. W. F.; Cassar, M. M.; Nistor, R. A. Ground State Energies for Helium, H⁻, and Ps⁻. *Phys. Rev. A* **2002**, *65*, 054501.
7. Wang, L. M.; Yan, Z. C.; Qiao, H. X.; Drake, G. W. F. Variational Energies and the Fermi Contact Term for the Low-Lying States of Lithium: Basis-Set Completeness. *Phys. Rev. A* **2012**, *85*, 052513.
8. Roothaan, C. C. J.; Weiss, A. W. Correlated Orbitals for the Ground State of Heliumlike Systems. *Rev. Mod. Phys.* **1960**, *32*, 194–205.
9. Pack, R. T.; Brown, W. B. Cusp Conditions for Molecular Wavefunctions. *J. Chem. Phys.* **1966**, *45* (2), 556–559. https://doi.org/10.1063/1.1727605.
10. Karwowski, J.; Pestka, G. Configuration Interaction Methods. *Comput. Methods Sci. Technol.* **1998**, *4*, 57–69.
11. Davidson, E. R. Configuration Interaction Wave Functions. In *Relativistic and Electron Correlation Effects in Molecules and Solids*; Malli, G. L., Ed.; Plenum Press: New York, 1994; pp. 105–131.
12. Sims, J. S.; Hagstrom, S. A. High-Precision Hy-CI Variational Calculations for the Ground State of Neutral Helium and Helium-Like Ions. *Int. J. Quantum Chem.* **2002**, *90* (6), 1600–1609.
13. Sims, J. S.; Hagstrom, S. A. One Center r_{ij} Integrals Over Slater-Type Orbitals. *J. Chem. Phys.* **1971**, *55* (10), 4699–4710. https://doi.org/10.1063/1.1675567.

14. Condon, E. U.; Shortley, G. H. *The Theory of Atomic Spectra*; Cambridge U. P.: Cambridge, England, 1963, https://doi.org/10.1126/science.116.3007.181-b.

15. Stanke, M.; Bubin, S.; Adamowicz, L. Lowest Ten Singlet P States of Beryllium Calculated With All-Electron Explicitly Correlated Gaussian Functions. *J. Phys. B.* **2019**, *52*, 155002. https://doi.org/10.1088/1361-6455/ab2510. article.

16. Hornyák, I.; Adamowicz, L.; Bubin, S. Ground and Excited ^{1}S States of the Beryllium Atom. *Phys. Rev. A* **2019**, *100*, 032504. https://doi.org/10.1103/PhysRevA.100.032504.

17. Pachucki, K.; Komasa, J. Gaussian Basis Sets With the Cusp Condition. *Chem. Phys. Lett.* **2004**, *389*, 209–211.

18. Pachucki, K.; Komasa, J. Three-Electron Integral in Gaussian Basis Set With Linear Terms. *Phys. Rev. A* **2004**, *70*, 022513.

19. Puchalski, M.; Komasa, J.; Pachucki, K. Testing Quantum Electrodynamics in the Lowest Singlet States of the Beryllium Atom. *Phys. Rev. A* **2013**, *87*, 030502. https://doi.org/10.1103/PhysRevA.87.030502.

20. Schwartz, C. Experiment and Theory in Computations of the He Atom Ground State. *Int. J. Mod. Phys. E* **2006**, *15* (4), 877–888.

21. Schwartz, C. Further Computations of the He Atom Ground State. *arXiv:math-ph* **2006**, 0605018.

22. Nakashima, H.; Nakatsuji, H. Solving the Schrödinger Equation for Helium Atom and Its Isoelectronic Ions With the Free Iterative Complement Interaction (ICI) Method. *J. Chem. Phys.* **2007**, *127* (22), 224104.

23. Hättig, C.; Klopper, W.; Köhn, A.; Tew, D. P. Explicitly Correlated Electrons in Molecules. *Chem. Rev.* **2012**, *112*, 4–74.

24. Ruiz, M. B. Hylleraas–Configuration Interaction Calculations on the $1\,^1$S Ground State of the Helium Atom. *J. Coord. Chem.* **2015**, *68* (17-18), 3340–3361. https://doi.org/10.1080/00958972.2015.1064907.

25. Rychlewski, J. *Explicitly Correlated Wave Functions in Chemistry and Physics. Theory and Applications*; Kluwer Academic Publishers: Dordrecht, Netherlands, 2003. https://doi.org/10.1007/978-94-017-0313-0.

26. Kutzelnigg, W. r_{12}-Dependent Terms in the Wave Function as Closed Sums of Partial Wave Amplitudes for Large *l*. *Theor. Chim. Acta* **1985**, *68*, 445–469. https://doi.org/10.1007/BF00527669.

27. Kong, L.; Bischoff, F.; Valeev, E. F. Explicitly Correlated R12/F12 Methods for Electronic Structure. *Chem. Rev.* **2012**, *112*, 75–107. https://doi.org/10.1021/cr200204r.

28. Gdanitz, R. J. Accurately Solving the Electronic Schrödinger Equation of Atoms and Molecules Using Explicitly Correlated (r_{12})-MR–CI. II. Ground-State Energies of First-Row Atoms and Positive Atomic Ions. *J. Chem. Phys.* **1998**, *109* (22), 9795–9801.

29. Jitrik, O.; Bunge, C. F. Atomic Configuration Interaction and Studies of He, Li, Be, and Ne Ground States. *Phys. Rev. A* **1997**, *56*, 2614–2623.

30. Bunge, C. F. Configuration Interaction Benchmark for Be Ground State. *Theor. Chem. Acc.* **2010**, *126*, 139–150.

31. Almora–Díaz, C. X.; Bunge, C. F. Nonrelativistic CI Calculations for B$^+$, B, and B$^-$ Ground States. *Int. J. Quantum Chem.* **2010**, *110* (15), 2982–2988.

32. Wright, J. S.; Barclay, V. J. Approaching the Exact Energy for H_2: Bond Functions vs Polarization Functions. *J. Chem. Phys.* **1987**, *86* (5), 3054–3055.

33. Sasaki, F.; Yoshimine, M. Configuration-Interaction Study of Atoms. I. Correlation Energies of B, C, N, O, F, and Ne. *Phys. Rev. A* **1974**, *9*, 17–25.

34. Rychlewski, J.; Cencek, W. Adiabatic Calculations Using Explicitly Correlated Wave Functions. In *Explicitly Correlated Wave Functions in Chemistry and Physics. Theory and Applications*; Rychlewski, J., Ed.; Kluwer Academic Publishers: Dordrecht, Netherlands, 2003; pp. 249–274.

35. Cencek, W.; Szalewicz, K. Ultra-High Accuracy Calculations for Hydrogen Molecule and Helium Dimer. *Int. J. Quantum Chem.* **2008**, *108* (12), 2191–2198.
36. Stanke, M.; Komasa, J.; Kedziera, D.; Bubin, S.; Adamowicz, L. Accuracy Limits on the Description of the Lowest S Excitation state in the Li Atom Using Explicitly Correlated Gaussian Basis Functions. *Phys. Rev. A.* **2008**, *78*, 052507.
37. Puchalski, M.; Komasa, J.; Pachucki, K. Explicitly Correlated Wave Function for a Boron Atom. *Phys. Rev. A* **2015**, *92*, 062501.
38. Strasburger, L. Explicitly Correlated Wave Functions of the Ground State and the Lowest Quintuplet State of the Carbon Atom. *Phys. Rev. A* **2019**, *99*, 069901.
39. Pachucki, K. Born-Oppenheimer Potential for H_2. *Phys. Rev. A* **2010**, *82*, 032509.
40. Büsse, G.; Kleindienst, H.; Lúchow, A. Nonrelativistic Energies for the Be Atom: Double-Linked Hylleraas-CI Calculation. *Int. J. Quantum Chem.* **1998**, *66*, 241–247.
41. Sims, J. S.; Hagstrom, S. A. High Precision Variational Calculations for the Born-Oppenheimer Energies of the Ground State of the Hydrogen Molecule. *J. Chem. Phys.* **2006**, *124*, 094101.
42. Sims, J. S.; Hagstrom, S. A. Hylleraas-Configuration-Interaction Study of the 2 ^{2}S Ground State of Neutral Lithium and the First Five Excited ^{2}S States. *Phys. Rev. A* **2009**, *80*, 052507.
43. Sims, J. S.; Hagstrom, S. A. Hylleraas-Configuration-Interaction Nonrelativistic Energies for the ^{1}S Ground States of the Beryllium Isoelectronic Sequence. *J. Chem. Phys.* **2014**, *140*, 224312. https://doi.org/10.1063/1.4881639.
44. Ruiz, M. B. Progress in Hylleraas-CI Calculations on Boron. In *Advances in the Theory of Quantum Systems in Chemistry and Physics, Progress in Theoretical Chemistry and Physics*; Hoggan, P., Ed.; Vol. 22; Springer, 2012; pp. 103–17.
45. Sims, J. S.; Padhy, B.; Ruiz, M. B. Exponentially Correlated Hylleraas–Configuration Interaction Nonrelativistic Energy of the ^{1}S Ground State of the Helium Atom. *Int. J. Quantum Chem.* **2021**, *121*, e26470. https://doi.org/10.1002/qua.26470.
46. Korobov, V. I. Nonrelativistic Ionization Energy for the Helium Ground State. *Phys. Rev. A* **2002**, *66*, 024501.
47. Puchalski, M.; Komasa, J. Nonadiabatic Rotational States of the Hydrogen Molecule. *Phys. Chem. Chem. Phys.* **2018**, *20*, 247–255.
48. Puchalski, M.; Kedziera, D.; Pachucki, K. Ground State of Li and Be$^+$ Using Explicitly Correlated Functions. *Phys. Rev. A* **2009**, *80*, 032521.
49. Aznabaev, D. T.; Bekbaev, A. K.; Korobov, V. I. Nonrelativistic Energy Levels of Helium Atoms. *Phys. Rev. A* **2018**, *98* (1), 012510.
50. Kurokawa, Y.; Nakashima, H.; Nakatsuji, H. Free Iterative-Complement-Iteration Calculations of the Hydrogen Molecule. *Phys. Rev. A* **2005**, *72*, 062502.
51. Puchalski, M.; Kedziera, D.; Pachucki, K. Ground State of Li and Be$^+$ Using Explicitly Correlated Functions. *Phys. Rev. A* **2010**, *82*, 062509.
52. Chakravorty, S. J.; Gwaltney, S. R.; Davidson, E. R.; Parpia, F. A.; Fischer, C. F. Ground-State Correlation Energies for Atomic Ions With 3 to 18 Electrons. *Phys. Rev. A* **1993**, *47* (5), 3649–3671.
53. Fock, V. On the Schrödinger Equation for the Helium Atom. *Izv. Akad. Nauk SSSR* **1954**, *18*, 161.
54. Nakatsuji, H.; Nakashima, H. Solving the Schrödinger Equation With the Free-Complement Chemical-Formula Theory: Variational Study of the Ground and Excited States of Be and Li Atoms. *J. Chem. Phys.* **2019**, *150*, 044105. https://doi.org/10.1063/1.5065565.
55. Nakashima, H.; Nakatsuji, H. Free Complement s_{ij}–Assisted r_{ij} Theory: Variational Calculation of the Quintet State of a Carbon Atom. *Phys. Rev. A* **2020**, *102*, 052835.
56. Hirschfelder, J. O. Removal of Electron-Electron Poles From Many-Electron Hamiltonians. *J. Chem. Phys.* **1963**, *39*, 3145–3146.

57. Thakkar, A. J. Comments on Explicitly Correlated Wave Functions for the Ground State of the Helium Atom. *Phys. Rev. A* **1977**, *16* (4), 1740–1742.

58. Slater, J. C. The Normal State of Helium. *Phys. Rev.* **1928**, *32*, 349–360.

59. Thakkar, A. J.; V.H. Smith. Compact and Accurate Integral–Transform Wave Functions. I. The 1 ^{1}S State of the Helium-Like Ions From H$^-$ Through Mg^{10+}. *Phys. Rev. A* **1977**, *15* (1), 1–15.

60. Harris, F. E. Exponentially Correlated Wave Functions for Four-Body Systems. *Adv. Quantum Chem* **2016**, *73*, 81–102.

61. Harris, F. E. Matrix Elements for Explicitly-Correlated Atomic Wave Functions. In *Concepts, Methods and Applications of Quantum Systems in Chemistry and Physics. Progress in Theoretical Chemistry and Physics*; Wang, Y., Thachuk, M., Krems, R., Maruani, J., Eds.; Vol. 31; Springer: New York, 2018.

62. King, F. W. High-Precision Calculations for the Ground and Excited States of the Lithium Atom. *Adv. At. Mol. Opt. Phys.* **1999**, *40*, 57–112.

63. King, F. W. Analysis of Some Integrals Arising in the Atomic Four-Electron Problem. *J. Chem. Phys.* **1993**, *99*, 3622–3628.

64. King, F. W.; Quicker, D.; Langer, J. Compact Wave Functions for the Beryllium Isoelectronic Series, Li$^-$ to Ne^{6+}: A Standard Hylleraas Approach. *J. Chem. Phys.* **2011**, *134*, 124114. https://doi.org/10.1063/1.3569565.

65. Sims, J. S.; Hagstrom, S. A. Combined Configuration Interaction–Hylleraas Type Wave Function Study of the Ground State of the Beryllium Atom. *Phys. Rev. A* **1971**, *4* (3), 908–916. https://doi.org/10.1103/PhysRevA.4.908.

66. Woźnicki, W. On the Method of Constructing the Variational Wave Functions for Many-Electron Atoms. In *Theory of Electronic Shells in Atoms and Molecules*; Jucys, A., Ed.; Mintis: Vilnius, 1971; pp. 103–106.

67. Wang, C.; Mei, P.; Kurokawa, Y.; Nakashima, H.; Nakatsuji, H. Analytical Evaluations of Exponentially Correlated Unlinked One-Center, Three- and Four-Electron Integrals. *Phys. Rev. A* **2012**, *85*, 042512.

68. Bylicki, M.; Bednarz, E. Nonrelativistic Energy of the Hydrogen Negative Ion in the $2p^2$ $^3P^e$ Bound State. *Phys. Rev. A* **2003**, *67*, 022503.

69. Larsson, S. Calculations on the ^{2}S Ground State of the Lithium Atom Using Wave Functions of Hylleraas Type. *Phys. Rev.* **1968**, *169* (1), 49–54.

70. Pipin, J.; Bishop, D. M. Accurate Variational Calculations of Energies of the 2 ^{2}S, 2 ^{2}P, and 3 ^{2}D States and the Dipole, Quadrupole, and Dipole-Quadrupole Polarizabilities and Hyperpolarizability of the Lithium Atom. *Phys. Rev. A* **1992**, *45* (5), 2736–2743.

71. Lüchow, A.; Kleindienst, H. Accurate Upper and Lower Bounds to the ^{2}S States of the Lithium Atom. *Int. J. Quantum Chem.* **1994**, *51* (4), 211–224.

72. Yan, Z. C.; Drake, G. W. F. Eigenvalues and Expectation Values for the $1s^22s$ ^{2}S, $1s^22p$ ^{2}P, and the $1s^23d$ ^{2}D States of Lithium. *Phys. Rev. A* **1995**, *52*, 3711–3717.

73. King, F. W. Progress on High-Precision Calculations for the Ground State of Atomic Lithium. *J. Mol. Struct. (Theochem)* **1997**, *400*, 7–56. https://doi.org/10.1016/S0166-1280(97)90265-7.

74. Komasa, J.; Rychlewski, J.; Jankowski, K. Benchmark Energy Calculations on Be-Like Atoms. *Phys. Rev. A* **2002**, *65*, 042507.

75. Komasa, J.; Cencek, W.; Rychlewski, J. Explicitly Correlated Gaussian Functions in Variational Calculations: The Ground State of the Beryllium Atom. *Phys. Rev. A* **1995**, *52*, 4500–4507.

76. Lüchow, A.; Kleindienst, H. Stable and Efficient Algorithm for Selected Eigenvalues and Eigenvectors of the General Symmetric Eigenproblem. *Comput. Chem.* **1993**, *17* (1), 61–66.

77 Merkens, H. P. Eigenwertberechnungen an Angeregten ^{1}S-Zuständen des Berylliumatoms. Ph.D. thesis, Heinrich Heine University of Düsseldorf, Düsseldorf 2002. Ph. D. dissertation (unpublished).

78 Büsse, G. Eigenwertberechnungen an Atomaren Fünf–Teilchen–Systemen. Ph.D. thesis, Heinrich Heine University of Düsseldorf, Düsseldorf 1998. Ph. D. dissertation (unpublished).

79. Löwdin, P. O. Angular Momentum Wavefunctions Constructed by Projector Operators. *Rev. Mod. Phys.* **1964**, *36*, 966–976. https://doi.org/10.1103/RevModPhys.36.966.

80. Cencek, W.; Komasa, J.; Rychlewski, J. Configuration Interaction and Hylleraas Configuration Interaction Methods in Valence Bond Theory. Diatomic Two-Electron Systems. *J. Chem. Phys.* **1991**, *95* (4), 2572–2576.

81. James, H. M.; Coolidge, A. S. On the Ground State of Lithium. *Phys. Rev.* **1936**, *49*, 688–695.

82. Drake, G. F. W. High Precision Calculations for Helium. In *Atomic, Molecular, and Optical Physics Handbook*; Drake, G. F. W., Ed.; API Press: New York, 1996; pp. 154–171.

83. Pluvinage, P. Fonction d'onde Approchée à un paramétre pour l'état Ondamental des Atomes à deux électrons. *Ann. Phys. (Paris)* **1950**, *12*, 145–152.

84. Walsh, P.; Borowitz, S. Application of Wave Functions Containing Interelectron Coordinates. II. Approximate Energy Levels of Atoms. *Phys. Rev.* **1960**, *119*, 1274.

85. Ruiz, M. B. Hylleraas Method for Many-Electron Atoms. I. The Hamiltonian. *Int. J. Quantum Chem.* **2005**, *101*, 246–260.

86. Ruiz, M. B. Evaluation of Hylleraas-CI atomic integrals by Integration Over the Coordinates of One Electron. I. Three-Electron Integrals. *J. Math. Chem.* **2009**, *46* (1), 24–64.

87. Ruiz, M. B. Analytic Evaluation of Hylleraas-CI Atomic Integrals by Integration over the Coordinates of One Electron. III. Two-Electron Kinetic Energy Integrals. *J. Math. Chem.* **2011**, *49* (10), 2457–2485.

88. Ruiz, M. B. Analytic Evaluation of Hylleraas-CI Atomic Integrals by Integration Over the Coordinates of One Electron. II. Four–Electron Integrals. *J. Math. Chem.* **2009**, *46*, 1322–1355.

89. Calais, J. L.; Löwdin, P. O. A Simple Method of Treating Atomic Integrals Containing Functions of r_{12}. *J. Mol. Spectrosc.* **1962**, *8*, 203–211.

90. Öhrn, Y.; Nordling, J. On the Calculation of Some Atomic Integrals Containing Functions of r_{12}, r_{13}, and r_{23}. *J. Chem. Phys.* **1963**, *39* (7), 1864–1872.

91. Kolos, W.; Roothaan, C. C. J. Accurate Electronic Wave Functions for the H_2 Molecule. *Rev. Mod. Phys.* **1960**, *32*, 219–232.

92. Ruiz, M. B. Evaluation of Hylleraas-CI Atomic Integrals by Integration Over the Coordinates of One Electron. IV. An Improved Algorithm for Three-Electron Kinetic Energy Integrals. *J. Math. Chem.* **2016**, *54*, 1083–1109.

93. Ruiz, M. B. Hylleraas Method for Many-Electron Atoms. II. Integrals Over Wave Functions With One Interelectronic Coordinate. *Int. J. Quantum Chem.* **2005**, *101*, 261–273.

94. Harris, F. E. Integrals Arising in Atomic Hylleraas Methods. *Mol. Phys.* **2017**, *115* (17), 1–4.

95. Harris, F. E. Kinetic-Energy Matrix Elements for Atomic Hylleraas Wave Functions. *J. Chem. Phys.* **2016**, *144*, 204110.

96. Harris, F. E. Atomic Electronic Structure Computations With Hylleraas-CI Wave Functions. *Adv. Quantum Chem.* **2018**, *76*, 187–210.

97. Harris, F. E. Matrix Elements for Explicitly-Correlated Atomic Wave Functions. In *Concepts, Methods and Applications of Quantum Systems in Chemistry and Physics. Progress in Theoretical Chemistry and Physics*; Wang, Y., Thachuk, M., Krems, R., Maruani, J., Eds.; Vol. 31; Springer: New York, 2018.

98. Sims, J. S.; Hagstrom, S. A. Comment: "Analytic Value of the Atomic Three-Electron Integral With Slater Wave Functions" [Phys. Rev. A 44,5492(1991)]. *Phys. Rev. A* **2003**, *68*, 016501.

99. Sims, J. S.; Hagstrom, S. A. Mathematical and Computational Science Issues in High Precision Hylleraas-Configuration Interaction Variational Calculations: I. Three-Electron Integrals. *J. Phys. B At. Mol. Opt. Phys.* **2004**, *37*, 1519–1540.

100. Sims, J. S.; Hagstrom, S. A. Mathematical and Computational Science Issues in High Precision Hylleraas-Configuration Interaction Variational Calculations: II. Kinetic Energy and Electron–Nucleus Interaction Integrals. *J. Phys. B: At. Mol. Opt. Phys.* **2007**, *40*, 1575–1587.

101. Sims, J. S.; Hagstrom, S. A. Mathematical and Computational Science Issues in High Precision Hylleraas-Configuration Interaction Variational Calculations: III. Four-Electron Integrals. *J. Phys. B At. Mol. Opt. Phys.* **2015**, *48*, 175003.

102. Forum, Message Passing Interface. MPI: A Message-Passing Interface Standard. *Int. J. Supercomput. Appl.* **1994**, *8* (3/4), 159–416.

103. Fromm, D. M.; Hill, R. N. Analytic Evaluation of Three-Electron Integrals. *Phys. Rev. A* **1987**, *36*, 1013–1044.

104. Levin, D. Development of Non-Linear Transformations for Improving Convergence of Sequences. *Int. J. Comput. Math. B* **1973**, *3*, 371–388.

105. Parlett, B. N. *The Symmetric Eigenvalue Problem*; SIAM: Philadelphia, 1998 (See Chapter 4).

106. Sims, J. S.; Ruiz, M. B. Parallel Generalized Real Symmetric-Definite Eigenvalue Problem. *J. Res. Natl. Inst. Stand. Technol.* **2020**, *125*, 125032. https://doi.org/10.6028/jres.125.032.

107. Pestka, G. Variational Solution of the Dirac-Coulomb Equation Using Explicitly Correlated Wavefunctions. Matrix Elements and Radial Integrals. *J. Phys. A Math. Gen.* **1998**, *31*, 6243–6251.

108. Pestka, G.; Karwowski, J. Dirac-Coulomb Hamiltonian in n-Electron Model Spaces. *Czechoslovak Chem. Commun.* **2003**, *68* (2), 275–294.

109. Bylicki, M. The Hermitian Representation of the Complex Rotation Method and its Application to the $1s2s^2\ ^2S$ Resonance of He$^-$. *J. Phys. B At. Mol. Opt. Phys.* **1991**, *24*, 413–421.

110. Bylicki, M. Spectrum of Doubly Excited $^4P^e$ Resonances in He$^-$. *J. Phys. B At. Mol. Opt. Phys.* **1997**, *30*, 189–201.

111. Bylicki, M.; Nicolaides, C. A. Energies and Widths of Triply Excited $n = 2$ Intrashell Autoionizing States of He$^-$. *Phys. Rev. A* **1995**, *51* (1), 204–210.

112. Frolov, A. M.; Ruiz, M. B. Atomic Excitations During the Nuclear β^- Decay in Light Atoms. *Phys. Rev. A* **2010**, *82*, 042511.

113. Sims, J. S.; Hagstrom, S. A. Combined Configuration-Interaction-Hylleraas Studies of Atomic States. III. The four Lowest ^2S and Four Lowest ^2P States of Lithium. *Phys. Rev. A* **1975**, *11* (3), 418–420.

114. Sims, J. S.; Hagstrom, S. A.; Rumble, J. R., Jr. Upper and Lower Bounds to Atomic and Molecular Properties. III. Lithium Oscillator Strengths for Various Doublet S - Doublet P Transitions. *Phys. Rev. A* **1976**, *13*, 242–250.

115. Sims, J. S.; Hagstrom, S. A.; J.R. Rumble, J. Upper and Lower Bounds to Atomic and Molecular Properties. IV. Electric Polarizabilities of Three-Electron Atoms by a Lower-Bound Procedure. *Phys. Rev. A* **1976**, *14*, 576–578.

116. Langhoff, P.; Corcoran, C. T.; Sims, J. S.; Weinhold, F.; Glover, R. Moment-Theory Investigations of Photoabsorption and Dispersion Profiles in Atoms and Ions. *Phys. Rev. A* **1976**, *14* (3), 1042–1056.

117. Langhoff, P.; snd J. S. Sims, C. T. C. Photoabsorption in Atomic Lithium. *Phys. Rev. A* **1977**, *16* (4), 1513–1520.

118. Pestka, G.; Woźnicki, W. Hylleraas-Type Calculations for Lithium. *Chem. Phys. Lett.* **1996**, *255*, 281–286.

119. Frolov, A. M.; Ruiz, M. B.; Wardlaw, D. M. Bound State Spectra and Properties of the Doublet States in Three-Electron Atomic Systems. *Chem. Phys. Lett.* **2014**, *608*, 191–200.

120. Ruiz, M. B.; Margraf, J. T.; Frolov, A. M. Hylleraas–Configuration Interaction Analysis of the Low-Lying States in the Three-Electron Li Atom and Be$^+$ Ion. *Phys. Rev. A* **2013**, *88*, 012505.

121. Ruiz, M. B.; Frolov, A. M. On the β^-–Decay in the ^{8}Li and ^{9}Li Atoms. *Adv. Quantum Chem.* **2013**, *67*, 267–289.

122. Bunge, C. F. Electronic Wave Functions for Atoms. I. Ground State of Be. *Phys. Rev.* **1968**, *168*, 92–103.

123. Puchalski, M.; Pachucki, K. Ground State Wave Function and Energy of the Lithium Atom. *Phys. Rev. A* **2006**, *73*, 022503.

124. Harris, F. E.; Frolov, A. M.; Smith, V. H., Jr. Exponential Variational Expansion in Relative Coordinates for Highly Accurate Bound State Calculations in Four-Body Systems. *J. Chem. Phys.* **2003**, *119*, 8833.

125. Stanke, M.; Kedziera, D.; Adamowicz, L. Lowest Excitation Energy of ^{9}Be. *Phys. Rev. Lett.* **2007**, *99*, 043001. https://doi.org/10.1103/PhysRevLett.99.043001.

126. Stanke, M.; Komasa, J.; Bubin, S.; Adamowicz, L. Five Lowest ^{1}S States of the Be Atom Calculated With a Finite-Nuclear-Mass Approach and With Relativistic and QED Corrections. *Phys. Rev. A* **2009**, *80*, 022514. https://doi.org/10.1103/PhysRevA.80.022514.

127. Sims, J. S.; Whitten, R. C. Upper and Lower Bounds to Atomic and Molecular Properties. I. Be-Sequence Oscillator Strengths (Dipole-Length Formulation) for the $1s^2\,2s^2\,^1$S – $1s^2\,2s2p\,^1$P Transition. *Phys. Rev. A* **1973**, *8*, 2220–2230.

128. Sims, J. S.; Rumble, J. R., Jr. Upper and Lower Bounds to Atomic and Molecular Properties. II. Electric Polarizabilities of Four-Electron Atoms by a Lower Bound Procedure. *Phys. Rev. A* **1973**, *8*, 2231–2235.

129. Sims, J. S.; Hagstrom, S. A. Hylleraas-Configuration Interaction Study of the ^{1}S Ground State of Neutral Beryllium. *Phys. Rev. A* **2011**, *83*, 032518. https://doi.org/10.1103/PhysRevA.83.032518.

130. Sims, J. S. Hylleraas-Configuration Interaction Study of the ^{1}S Ground State of the Negative Li Ion. *J. Phys. B At. Mol. Opt. Phys.* **2017**, *50*, 245003.

131. Sims, J. S. Hylleraas–Configuration Interaction (Hy-CI) Non-Relativistic Energies for the 3 ^{1}S, 4 ^{1}S, 5 ^{1}S, 6 ^{1}S, and 7 ^{1}S Excited States of the Beryllium Atom. *J. Res. Natl. Inst. Stand. Technol.* **2020**, *125*, 125006. https://doi.org/10.1088/1361-6455/aa961e.

132. Zhang, Y. Z.; Gao, Y. C.; Jiao, L. G.; Liu, F.; Ho, Y. K. Linear Dependence in Hylleraas-Configuration Interaction Calculations of He Atom. *Int. J. Quantum Chem.* **2019**, *120*, e26136. https://doi.org/10.1002/qua.26136.

133. Padhy, B. Kinetic Energy Matrix Elements for a Two-Electron Atom With Extended Hylleraas-CI Wave Function. *Orissa J. Phys.* **2018**, *25* (1), 9–21.

134. Padhy, B. Analytic Evaluation of Two-Electron Atomic Integrals Involving Extended Hylleraas-CI Functions With STO Basis. *Orissa J. Phys.* **2018**, *25* (2), 99–112.

135. Frankowski, K.; Pekeris, C. L. Erratum: Logarithmic Terms in the Wave Functions of the Ground State of Two-Electron Atoms. *Phys. Rev.* **1966**, *150*, 366(E).

136. Freund, D. E.; Huxtable, B. D.; Morgan, J. D., III. Variational Calculations on the Helium Isoelectronic Sequence. *Phys. Rev. A* **1984**, *29*, 980–982.

137. Thakkar, A. J.; Koga, T. Ground State Energies for the Helium Isoelectronic Sequence. *Phys. Rev. A* **1994**, *50*, 854–856.

138. Korobov, V. I. Coulomb Three-Body Bound-State Problem: Variational Calculations of Nonrelativistic Energies. *Phys. Rev. A* **2000**, *61*, 064503.

139. Clary, D. C. Configuration-Interaction-Hylleraas Calculations on One-Positron Atomic Systems. *J. Phys. B Atom. Mol. Phys.* **1976**, *9* (17), 3115–3129.

140. Clary, D. C. Variational Calculations on Many-Electron Diatomic Molecules Using Hylleraas-Type Wavefunctions. *Mol. Phys.* **1977**, *34* (3), 793–811.

141. Clary, D. C.; Handy, N. C. CI-Hylleraas Variational Calculation on the Ground State of the Neon Atom. *Phys. Rev. A* **1976**, *14* (5), 1607–1613.

142. Clary, D. C.; Handy, N. C. Hylleraas-Type Wavefunction for Lithium Hydride. *Chem. Phys. Lett.* **1977**, *51*, 483–486.

143. Frye, D.; Lie, G. C.; Chakravorty, S. J.; Preiskorn, A.; Clementi, E. Hylleraas-Configuration Interaction Method Using Gaussian Functions. In *Modern Techniques in Computational Chemistra-89*; Clementi, E., Ed.; ESCOM: Leiden, 1989; pp. 207–241.

144. Preiskorn, A.; Lie, G. C.; Frye, D.; Clementi, E. Gaussian Functions in Hylleraas-Configuration Interaction Calculations. Potential Curves for the $e\ ^3\Sigma_u^+$ and the $f\ ^3\Sigma_u^+$ States of Hydrogen. *J. Chem. Phys.* **1990**, *92*, 4941–4947.

145. Preiskorn, A.; Frye, D.; Clementi, E. Gaussian Functions in Hylleraas-Configuration Interaction Calculations. VI. The First Excited State of H_3^+. *J. Chem. Phys.* **1991**, *94*, 7204–7207.

146. Rychlewski, J. Explicitly Correlated Functions in Molecular Quantum Chemistry. *Adv. Quantum Chem.* **1998**, *31*, 173–199.

147. Preiskorn, A.; Woźnicki, W. Superposition of Correlated Configurations Method. The Ground State of H_3^+. *Chem. Phys. Lett.* **1982**, *86*, 369–373.

148. Preiskorn, A.; Woźnicki, W. Variational Calculations for the Ground State of H_3^+. *Mol. Phys.* **1984**, *52* (6), 1291–1301.

149. Piszczatowski, K.; Lach, G.; Jeziorski, B.; Przybytek, M.; Komasa, J.; Pachucki, K. Theoretical Determination of the Dissociation Energy of Molecular Hydrogen. *J. Chem. Theory Comp.* **2009**, *5*, 3039–3048.

150. Ruiz, M. B.; Schumann, R. The Hamiltonian for Molecules in Interparticle Coordinates. *Chem. Phys. Lett.* **2005**, *406*, 1–9.

151. Ruiz, M. B.; Peuker, K. Mathematical Techniques in Molecular Calculations Using Slater Orbitals. In *Recent Advances in Computational Chemistry: Molecular Integrals Over Slater Orbitals*; Ozdogan, T., Ruiz, M. B., Eds.; Transworld Research Network: Kerala, India, 2008; pp. 99–144.

152. Ozdogan, T.; Ruiz, M. B. *Recent Advances in Computational Chemistry: Molecular Integrals over Slater Orbitals*; Transworld Research Network: Kerala, India, 2008.

153. Hoggan, P. E.; Ruiz, M. B.; Ozdogan, T. Molecular Integrals Over Slater-Type Orbitals. From Pioneers to Recent Progress. In *Quantum Frontiers of Atoms and Molecules in Physics, Chemistry and Biology*; Putz, M. V., Ed.; Vol. 22; Nova Science Publishers, Inc.: New York, 2010; pp. 69–90.