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Uncoupling correlated calculations in atomic physics: Very high accuracy and ease

S. P. Goldman
Department of Physics, The University of Western Ontario, London, Ontario, Canada N6A 3K7

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An uncoupled correlated variational method (i.e., explicitly using the interelectronic coordinates) for calculations involving several electrons is introduced. All the overlap and Hamiltonian matrix elements, including those involving the electron-electron interaction, are simple products of one-dimensional integrations. Although simple to implement, the method yields the best available energy for the ground state of the He zeroth-order Hamiltonian $H_0 = H_1 + H_2 + 1/r_{12}$. Preliminary nonoptimized and nonextrapolated calculations yield $E = -2.903\,724\,377\,034\,119\,593\,8(50)$ a.u. [S1050-2947(98)50402-7]

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I. INTRODUCTION

Correlated basis sets offer the most accurate results for calculations involving two or three electrons. The pioneering work of Pekeris and collaborators was for a long time the landmark for these types of calculations. In the original work of Pekeris [1], perimetric coordinates were used, these being linear combinations of the electron coordinates r_1 and r_2 and the interelectron coordinate r_{12}. In terms of these coordinates the integrals uncoupled into three infinite one-dimensional integrations that could easily be handled by the computer systems then available, using orthogonal Laguerre (orthogonal combinations of Slater-type) basis functions to analytically calculate matrix elements. Since this exceptional work appeared, new accuracy demands have been progressively placed on these energy calculations by improved experimental precision as well as accurate calculations of relativistic and quantum electrodynamics effects. As a result, a number of different correlated methods were introduced. Pekeris's group abandoned perimetric coordinates in favor of nonorthogonal Hylleraas basis sets in order to improve accuracy. Since then correlated methods have made direct use of the Hylleraas [2] coordinates r_1, r_2, and r_{12} within different strategies. The common factor among these calculations is the presence of multidimensional integrations, given the coupling of the limits of integration due to the coordinate $|r_1 - r_2| \leq r_{12} \leq r_1 + r_2$. The presence of these coupled integrations precludes orthogonal or band-diagonal overlap matrices for Slater-type basis functions; as a consequence, their accuracy is limited by the onset of numerical linear dependence. For Slater-based calculations the convergence can be improved and numerical dependence can be mitigated by the use of multiple exponential parameters, as shown for Slater relativistic Dirac-Hartree-Fock calculations in many-electron systems [3]. When applied to correlated calculations, the multiexponential approach has yielded the most accurate numbers to date [4,5].

In this paper we shall show that the accuracy of these calculations can be *exceeded* by a very simple computational method. We start with a short review of correlated variational methods.

II. CORRELATED CALCULATIONS

Correlated calculations derive their power from the fact that the interelectronic potential is not expanded in an infinite series, such as, for example, the infinite spherical expansion commonly used in configuration-interaction (CI) calculations. This is accomplished by a change in the coordinate system used and the corresponding volume element used in the integrations. A typical integral in CI or Hartree-Fock calculations is of the standard spherical type

$$I = \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \int_0^\pi \sin\theta_1 d\theta_1 \int_0^\pi \sin\theta_2 d\theta_2 \times \int_0^{2\pi} d\varphi_1 \int_0^{2\pi} d\varphi_2 f(\mathbf{r}_1, \mathbf{r}_2, r_{12}). \tag{1}$$

This integral can only be handled by a spherical (infinite) expansion of r_{12}. This makes the inclusion in the basis set of functions that depend explicitly on r_{12} difficult to implement.

In correlated methods the explicit use of r_{12} is facilitated by changing the integration volume element so that now the integrals are of the form [5]

$$I=\int_0^\infty r_1 dr_1 \int_0^\infty r_2 dr_2 \int_{|r_1-r_2|}^{r_1+r_2} r_{12} dr_{12} \times \int_0^\pi \sin\theta_1 d\theta_1 \int_0^{2\pi} d\varphi_1 \int_0^{2\pi} d\chi f(\mathbf{r}_1, r_2, r_{12}, \chi), \quad (2)$$

where χ is the angle of rotation around $\hat{\mathbf{r}}_1$ of the plane defined by $\hat{\mathbf{r}}_1$ and $\hat{\mathbf{r}}_2$. All the angular integrals involving θ_2 and φ_2 (now dependent variables) can be expressed in terms of $\cos\theta_{12}$, where θ_{12} is the interelectronic angle, given in terms of the independent variables by

$$\cos\theta_{12}=\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2=\frac{r_1^2+r_2^2-r_{12}^2}{2r_1r_2}. \quad (3)$$

We deal in this paper with the solutions to the two-electron nonrelativistic Hamiltonian with an infinite nuclear mass, which we call H_0. This is a Hamiltonian that has been the subject of extensive work in the literature and on which substantial emphasis has been placed in order to obtain very accurate solutions. The finite mass corrections can be accounted for by an overall scaling of the energy by the ratio of the electron and reduced masses and by the inclusion of mass polarization effects done perturbatively. The Hamiltonian H_0 provides an excellent (standard) test of the accuracy that different basis sets are able to achieve.

In terms of the spherical coordinates of each electron, the Hamiltonian H_0, in a.u. (a.u. will be used throughout this paper), is given by the expression

$$H_0=-\frac{1}{2}\nabla_{\mathbf{r}_1}^2-\frac{1}{2}\nabla_{\mathbf{r}_2}^2-\frac{Z}{r_1}-\frac{Z}{r_2}+\frac{1}{r_{12}}. \quad (4)$$

For two-electron S states, in terms of the coordinates defined for the integration (2), H_0 becomes

$$H_0=-\frac{1}{2r_1}\frac{\partial^2}{\partial r_1^2}r_1-\frac{1}{2r_2}\frac{\partial^2}{\partial r_2^2}r_2-\frac{1}{r_{12}}\frac{\partial^2}{\partial r_{12}^2}r_{12} +\frac{r_2\cos\theta_{12}-r_1}{r_{12}}\frac{\partial^2}{\partial r_1\partial_{12}}+\frac{r_1\cos\theta_{12}-r_2}{r_{12}}\frac{\partial^2}{\partial r_2\partial_{12}}-\frac{Z}{r_1} -\frac{Z}{r_2}+\frac{1}{r_{12}}, \quad (5)$$

where $\cos\theta_{12}$ is given by the expression of Eq. (3). The general form of H_0 for states with $L>0$ can be found in Ref. [5].

Typical correlated basis sets in the literature for calculations involving the Hamiltonian (5) are of the following forms: we start with the basis set using perimetric coordinates introduced by the ground breaking work of Pekeris and co-workers [1]

$$\varphi_i(r_1,r_2,r_{12})=e^{-\lambda(2\alpha+\beta+\gamma)}L_1(\alpha)L_2(\beta)L_3(\gamma), \quad (6)$$

where α, β, and γ are the perimetric coordinates

$$\alpha=r_1+r_2-r_{12},$$
$$\beta=r_1-r_2+r_{12}, \quad (7)$$
$$\gamma=-r_1+r_2+r_{12}.$$

This basis set took advantage of the fact that with these linear combinations of the radial variables the radial integrals uncouple into three independent integrations from 0 to ∞. Using generalized Laguerre polynomials for the functions L_i, the basis functions can also be made orthogonal. All these features point to great stability and speed of calculation. The basis set is, however, limited to a single nonlinear parameter (λ), limiting its ability to produce results of great accuracy. The same group later opted to relinquish the orthogonality and uncoupled properties in favor of a better convergence by introducing in the basis set features pointed out by the Fock expansion of the helium wave function. This involves including logarithmic and noninteger powers in the basis set [6–9]. This type of basis set has been the subject of intensive research until recently and is of the general form

$$\varphi_i(r_1,r_2,r_{12})=e^{-\lambda s}(\ln s)^k(s^2+t^2)^{n/2}P_1(s)P_2(t)P_3(u), \quad (8)$$

where k and n are integers, the P_i are usually integer powers of the arguments, and

$$s=r_1+r_2,\quad t=r_2-r_1,\quad u=r_{12}. \quad (9)$$

Another type of correlated radial basis set is of the form

$$\varphi_i(r_1,r_2,r_{12})=e^{-\xi_i r_1-\eta_i r_2}R_1(r_1)R_2(r_2)R_3(r_{12}), \quad (10)$$

where the R_i are usually positive integer powers of the arguments. This approach derives its convergence power by using multiple sets of the nonlinear parameters ξ and η, in this way also minimizing the numerical dependence problems typical of the Slater-type functions (10) [4].

The methods (8) and (10) have been the most widely used in recent years with the aim of obtaining the best possible accuracy. Common to these methods is the fact that the calculation of the matrix elements involves *coupled* integrations.

III. UNCOUPLED CORRELATED CALCULATIONS

The aim of this paper is to present a different approach that simplifies the calculations and yields high stability and accuracy. The inspiration for this method comes from the modified configuration-interaction (MCI) [10] and radially uncoupled configuration-interaction (RUCI) [11] approaches to configuration-interaction calculations, particularly the RUCI uncoupling of the radial integrals. The radial portion of the integral (2) can be rewritten in the following way:

$$J=\int_0^\infty r_1dr_1\int_0^\infty r_2dr_2\int_{|r_1-r_2|}^{r_1+r_2}r_{12}dr_{12}g(r_1,r_2,r_{12}) =\int_0^\infty r_>dr_>\int_0^{r_>}r_<dr_<\int_{r_>-r_<}^{r_>+r_<}r_{12}dr_{12}g(r_>,r_<,r_{12}) +\int_0^\infty r_>dr_>\int_0^{r_>}r_<dr_<\int_{r_>-r_<}^{r_>+r_<}r_{12}dr_{12}g(r_<,r_>,r_{12}), \quad (11)$$

TABLE I. Variational energy values in a.u. obtained in the present work. N_u, N_v, N_w are the number of one-dimensional basis functions of each type used. N_{uvw} is the largest value of the sum of the orders of U_i, V_i, and W_i, while N_{vw} is the largest value of the sum of the orders of V_i and W_i. N is the total number of vectors in the basis set.

N_u	N_v	N_w	N_{uvw}	N_{vw}	N	E (a.u.)
36	18	10	48	16	1943	−2.903 724 377 034 078
40	20	11	48	18	2676	−2.903 724 377 034 115 8
42	20	12	50	19	3468	−2.903 724 377 034 118 35
48	20	12	50	20	3792	−2.903 724 377 034 119 249
51	20	12	58	20	4262	−2.903 724 377 034 119 414
56	20	12	64	20	4652	−2.903 724 377 034 119 507 9
63	23	14	74	23	6636	−2.903 724 377 034 119 569 7
71	23	14	83	23	7328	−2.903 724 377 034 119 586 99
76	23	14	88	23	7738	−2.903 724 377 034 119 591 63
80	23	14	92	23	8066	−2.903 724 377 034 119 593 82

where

$$r_> = \max\{r_1, r_2\} \quad \text{and} \quad r_< = \min\{r_1, r_2\}. \qquad (12)$$

In other words, all the calculations require the integration

$$I = \int_0^\infty r_> dr_> \int_0^{r_>} r_< dr_< \int_{r_>-r_<}^{r_>+r_<} r_{12} dr_{12} g(r_>, r_<, r_{12}). \qquad (13)$$

In the RUCI method, the first two limits of integration are uncoupled by the change of variables

$$u = r_>, \quad v = r_< / r_>, \qquad (14)$$

which also has the advantage of explicitly introducing in the basis functions the ratio $r_< / r_>$ appearing in the spherical expansion of $1/r_{12}$. The uncoupling in the correlated case is completed by the new variable

$$w = \frac{r_{12} - r_>}{r_<}. \qquad (15)$$

With the new variables (14), (15), the integral (13) is rewritten as

$$I = \int_0^\infty u^5 du \int_0^1 v\, dv \int_{-1}^1 (1 + vw) dw f(u,v,w). \qquad (16)$$

If the function f in the integrand is of the form

$$f(u,v,w) = U(u) V(v) W(w), \qquad (17)$$

then the integral (16) fully uncouples into products of three one-dimensional integrations:

$$I = \int_0^\infty U(u) u^5 du \left\{ \int_0^1 V(v) v\, dv \int_{-1}^1 W(w) dw + \int_0^1 V(v) v^2 dv \int_{-1}^1 W(w) w\, dw \right\}. \qquad (18)$$

Full advantage of this decoupling is achieved by choosing a radial basis set of the form

$$\varphi_i = U_i(u) V_i(v) W_i(w). \qquad (19)$$

With this basis set all the overlap and Hamiltonian matrix elements are written as products of one-dimensional integrations of the form (18). Notice that the *choice* of the one-dimensional basis functions is arbitrary; one could, for example, use B splines, for which the one-dimensional nature of the calculations is particularly well suited. The simplest basis functions to choose would be Slater functions for the U_i and simple powers for the V_i and the W_i. Notice that, unlike the case of perimetric coordinates, there is no limitation on the number of nonlinear parameters one can introduce for any of the one-dimensional basis functions.

The Hamiltonian itself is easily rewritten in terms of the new coordinates using

$$\begin{aligned} r_1 &= u(\Theta + v\overline{\Theta}), \\ r_2 &= u(\overline{\Theta} + v\Theta), \\ r_{12} &= u(1 + vw), \end{aligned} \qquad (20)$$

where Θ is the Heaviside step function

$$\Theta = \Theta(r_1 - r_2) = \begin{cases} 1 & \text{if} \quad r_1 \geqslant r_2, \\ 0 & \text{if} \quad r_1 < r_2, \end{cases}$$

and

$$\overline{\Theta} = 1 - \Theta.$$

Use of the new variables u, v, and w introduces in the basis set an improvement in representing the cusp in the wave function at $r_1 = r_2$ in two ways: by using r_{12} explicitly as well as by using the variables $r_>$ and $r_<$. The latter, upon substitution in the Laplacian operators, introduces in the Hamiltonian operator Dirac delta functions $\delta(r_1 - r_2)$.

There is, however, a drawback with this kind of representation. Notice that a basis set of the form (19) can represent an exponential asymptotic decay only through the functions U_i by including functions of the form $e^{-\alpha u} u^p$. In other words, only the correct asymptotic behavior of $r_>$ can be rigorously included in the basis set. Any single radial basis function cannot be written as a product of two radial hydrogenic functions given that $e^{\beta r_<} = e^{auv}$ cannot be written as product of the form $f(u) g(v)$. The Taylor expansion of e^{auv}, however, *is* a linear combination of products $f_i(u) g_i(v)$, so that the correct asymptotic (hydrogenic) limit can be represented by a linear combination of the basis functions (19). It is crucial then to check the radial convergence in the radial hydrogenic limit. This has been done in Ref. [11] with excellent results, yielding the most accurate (by several orders of magnitude) CI radial limit in the literature. There is a price to pay, which is an increase in the size of the basis set.

In the present work the basis sets used are based on orthogonal polynomials suited to the domains of integration of the each of the integrals. For the U_i we use

$$U_i(u)=N_i e^{-\alpha_i u} L^{5}_{k_i}(2\alpha_i U), \tag{21}$$

where L^i_j is a generalized Laguerre polynomial, N_i is a normalization constant, and the α_i are arbitrary (variational) parameters. By choosing a set with a single parameter α, the basis set U_i is orthonormal. The overall overlap matrix is then made up of a set of block-diagonal arrays, one for each order of the Laguerre polynomials. As a result, the overlap matrix is easily and quickly diagonalized. For the one-dimensional basis functions V_i and W_i, Jacobi polynomials were used, making the overlap matrices for the V_i and the W_i narrowly band diagonal.

The Hamiltonian matrix elements are quickly calculated, as only values within the small one-dimensional basis sets need to be calculated. The Hamiltonian matrix is then constructed by taking products of these. In the present work, the size of the basis sets used is constrained, for specific sizes of the one-dimensional basis sets, by limiting the maximum value of the sum of the orders of V_i and W_i, as well as of U_i, V_i, and W_i. An enormous advantage of using orthogonal polynomials for the basis functions is the very high numerical stability of the calculations, which show no sign of numerical dependence even for very large basis sets. This stability allows one to accelerate the Hamiltonian diagonalization when more than a 13-digit accuracy is required and quadruple precision calculations are necessary. The Hamiltonian can be first diagonalized in double precision and the resulting eigenvector can be used as a (close) starting point for a quadruple precision search of the eigenvalue. Again, this can be only done, given that, with this basis set, a diagonalization in double precision, even with huge basis sets, does not fail.

In Table I we present results obtained with different basis-set sizes. These are preliminary values and no attempt has been made to optimize the basis set used. The result in the last row is our best nonextrapolated value for the ground state of He. The large number of vectors points to the stability of the method, as a double precision calculation will still succeed for these large dimensions, even though only 13 digits will then be obtained. The calculations are easy and quick; the results to full double precision accuracy can be easily obtained on a notebook PC. There are several reasons for the large number of basis functions. (i) A fundamental reason is related to the fact that the asymptotic hydrogenic limit is not incorporated in the basis set. (ii) Only one nonlinear parameter has been used in the basis set, namely, the exponential parameter of the functions U_i; the choice of a single parameter was made in favor of keeping the U_i orthogonal. Notice that nonlinear parameters can be introduced in the other one-dimensional basis functions too; for example, as weights of the orthogonal Jacobi polynomials. (iii) No attempt has been made (yet) to optimize the basis set. It is, however, remarkable that an extreme degree of accuracy is attainable by a method that is intrinsically very simple. Work is currently in progress on the optimization of the dimensionality. A drastic reduction in the size of the basis functions appears possible, as well as the rigorous incorporation of the asymptotic (hydrogenic) behavior in the basis set. The results of this ongoing work are to appear in a comprehensive paper. Future work will concentrate on the application of the method to three-electron systems (for which the extension is immediate) and QED calculations in two- and three-electron atoms for which the speed, ease, high numerical stability, and accuracy of the method are perfectly suited.

TABLE II. Comparison of the ground-state energy obtained in the present work with nonextrapolated previous results in the literature. E denotes the energy in a.u. N denotes the number of basis functions used.

	N	E (a.u.)
Frankowski and Pekeris [6]	246	$-2.903\,724\,377\,032\,6$
Freund *et al.* [8]	230	$-2.903\,724\,377\,034\,0$
Thakkar and Koga [9]	308	$-2.903\,724\,377\,034\,114\,4$
Drake and Yan [4]	1262	$-2.903\,724\,377\,034\,119\,479$
This work	8066	$-2.903\,724\,377\,034\,119\,593\,8(50)$

In Table II we present a comparison of the present work with previous non-extrapolated results in the literature.

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