# Coulomb three-body bound-state problem: Variational calculations of nonrelativistic energies

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It is known that variational methods are the most powerful tool for studying the Coulomb three-body bound-state problem. However, they often suffer from loss of stability when the number of basis functions increases. This problem can be cured by applying the multiprecision package designed by D. H. Bailey. We consider variational basis functions of the type $\exp(-\alpha_n r_1 - \beta_n r_2 - \gamma_n r_{12})$ with complex exponents. The method yields the best available energies for the ground states of the helium atom and the positive hydrogen molecular ion as well as many other known atomic and molecular systems.

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The development of the variational method for the Coulomb bound-state problem can be traced using as an example the ground state of the helium atom. In early days when computers were big and very expensive, the search proceeded mainly in the direction of making the expansion of the variational wave function as compact as possible (in the sense of the number of variational parameters and/or basis sets). At first, an explicitly correlated basis was introduced [1,2], now called the Hylleraas basis,

$$\psi(\mathbf{r}_1,\mathbf{r}_2) = e^{-1/2s} \sum c_{lmn} s^l u^m t^m,$$

$$s = r_1 + r_2, \quad u = r_{12}, \quad t = -r_1 + r_2; \quad (1)$$

then it became clear that at least for the ground state of the helium atom it is essential to incorporate into the wave function such peculiarities as logarithmic behavior of the type $R \ln R$ at $R = (r_1^2 + r_2^2)^{1/2} \to 0$, first analytically derived by Bartlett and Fock [3]. In 1966, Frankowski and Pekeris (see Table II below) introduced a compact representation [4] of the form

$$\psi(\mathbf{r}_1,\mathbf{r}_2) = e^{-\kappa s} \sum c_{lmnij} s^l u^m t^{2m} (s^2 + t^2)^{i/2} (\ln s)^j, \quad (2)$$

and later, in 1984, Freund and co-workers [5] reported an even more compact expansion of the same form. Inclusion of the logarithmic term into the variational wave function caused substantial improvement in the nonrelativistic energies for two-electron atoms. In 1994, Thakkar and Koga [6] found a compact expansion without logarithms which uses

powers that are not integers or even half integers. As far as we know, none of these compact expansions has been used for analytical evaluation of the matrix elements of the Breit interaction.

With the advance of computer power, basis sets became simplified, which allowed for calculation of the numerous matrix elements required for relativistic and QED corrections. Efforts were concentrated on a strategy that defines the sequence of basis functions generated. In [7] the double basis set method with generalized Hylleraas basis functions

$$\psi(\mathbf{r}_1,\mathbf{r}_2) = \sum c_{ijk}^A r_1^i r_2^j r_{12}^k e^{-\alpha_A r_1 - \beta_A r_2}$$

$$+ \sum c_{ijk}^B r_1^i r_2^j r_{12}^k e^{-\alpha_B r_1 - \beta_B r_2} \quad (3)$$

was used. This double basis set technique along with full optimization of nonlinear parameters for each basis set yields substantial progress in accuracy. However, further advance is hindered by numerical instability even in quadruple precision arithmetic due to the almost linear dependence of the basis set at large $N$.

The work of Goldman [8] is somewhat apart from the main path. It recovers the idea of Pekeris [2] of using uncoupled coordinates and orthogonal Laguerre and Jacoby polynomials as basis functions.

The method expounded in our work is a continuation of efforts by Drake and Yan [7] to utilize as simple basis func-

TABLE I. Variational energy (in a.u.) of the helium ground state as a function of $N$, the number of basis functions.

| $N$ | $E$ (a.u.) |
|---|---|
| 1400 | $-2.90372437703411959629$ |
| 1600 | $-2.903724377034119597843$ |
| 1800 | $-2.90372437703411195981964$ |
| 2000 | $-2.90372437703411195982713$ |
| 2200 | $-2.90372437703411195982955$ |
| Extrapolation | $-2.903724377034119598306(10)$ |

TABLE II. Comparison of the ground-state energy of the helium atom obtained in this work with other theoretical calculations.

| | $N$ | $E$ (a.u.) |
|---|---|---|
| Frankowski and Pekeris [4] | 246 | $-2.9037243770326$ |
| Freund, Huxtable, and Morgan [5] | 230 | $-2.9037243770340$ |
| Thakkar and Koga [6] | 308 | $-2.9037243770341144$ |
| Drake and Yan [7] | 1262 | $-2.90372437703411948$ |
| Goldman [8] | 8066 | $-2.903724377034119594$ |
| Drake [7] | 2114 | $-2.903724377034119596$ |
| This work | 2200 | $-2.903724377034119598296$ |

TABLE III. Variational energy (in a.u.) of the positive hydrogen ion ground state as a function of $N$, the number of basis functions.

| $N$ | $E$ (a.u.) |
|---|---|
| 1400 | $-0.597139063123404975$ |
| 1600 | $-0.597139063123405047$ |
| 1800 | $-0.5971390631234050655$ |
| 2000 | $-0.5971390631234050710$ |
| 2200 | $-0.5971390631234050740$ |
| Extrapolation | $-0.597139063123405076(2)$ |

TABLE IV. Comparison of the ground-state energy of the positive hydrogen molecular ion obtained in this work with other theoretical calculations. $m_p = 1836.152\,701 m_e$.

| | $N$ | $E$ (a.u.) |
|---|---|---|
| Grémaud, Delande, and Billy [15] | 31746 | $-0.597139063123$ |
| Rebane and Filinsky [16] | | $-0.59713906312340$ |
| Moss [17] | | $-0.5971390631234$ |
| This work | 2200 | $-0.597139063123405074$ |

tions (geminals) as possible, The expansion we want to consider is very similar to the generalized Hylleraas basis set, but instead of using polynomials over Hylleraas variables we generate nonlinear parameters in the exponents in a quasirandom manner,

$$r_1^{l_i} r_2^{m_i} r_{12}^{n_i} e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}} \Rightarrow e^{-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_{12}}. \quad (4)$$

This method has been successfully used in calculations [9,10] previously. Obviously, the matrix elements can be evaluated in the same way as for the generalized Hylleraas basis set (4). Moreover, if one replaces real exponents by complex exponents the integrals will remain exactly the same as for the real case. In its strategy the method is very close to the stochastic variational method by Varga and Suzuki [11], where Gaussians are exploited instead.

In a formal way, the variational wave function is expanded in the form

$$\psi_0 = \sum_{i=1}^{\infty} \{ U_i \,\mathrm{Re}[\exp(-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_{12})]$$

$$+ W_i \,\mathrm{Im}[\exp(-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_{12})] \} \mathcal{Y}_{l_1 l_2}^{LM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2). \quad (5)$$

Here $\alpha_i$, $\beta_i$, and $\gamma_i$ are complex parameters generated in a quasirandom manner [13,14]:

$$\alpha_i = \lfloor \tfrac{1}{2} i(i+1) \sqrt{p_\alpha} \rfloor [(A_2 - A_1) + A_1]$$

$$+ i \{ \lfloor \tfrac{1}{2} i(i+1) \sqrt{q_\alpha} \rfloor [(A_2' - A_1') + A_1'] \}. \quad (6)$$

$\lfloor x \rfloor$ designates the fractional part of $x$, $p_\alpha$, and $q_\alpha$ are some prime numbers, and $[A_1, A_2]$ and $[A_1', A_2']$ are real variational intervals which need to be optimized. The parameters $\beta_i$ and $\gamma_i$ are obtained in a similar way.

An important feature of the method is that it demonstrates a very fast convergence. The general rule that can be inferred experimentally from use of the method is that increasing the basis by about 200 functions yields about one additional digit in the variational energy. The minor deficiency is that the basis quickly degenerates as $N$ increases. Already for moderate $N \sim 250$–$400$ quadruple precision is required.

A multiprecision package of FORTRAN routines, MPFUN, has been designed by David H. Bailey [12] for computations with floating point numbers of an arbitrary length. Usually it

is necessary to make significant changes in the FORTRAN source code if FORTRAN-77 language is used. Fortunately, the author of the MPFUN package has developed a translator program that greatly facilitates converting the programs to multiprecision. In general, two directives incorporated as comments in a source code are required per one routine. For example, a source code for the variational method considered has been transformed to a multiprecision version within two hours of manual work. Eventually the code we obtained was tested on a personal computer with a Celeron 500 MHz processor. For one run with a basis of $N = 1400$ functions and 40 decimal digits it requires about 3 h. For users of FORTRAN-90 no preprocessor is needed due to new advanced features of FORTRAN-90, such as derived data types and operator extensions.

In our calculations for the helium ground state, four basis sets with independently optimized nonlinear parameters were used. These sets were built up like a pine tree. The first layer was tuned to approximate the general behavior of the solution at intermediate and large $r_1$ and $r_2$. The second layer was chosen to be flexible in a smaller region of $r_1$ and $r_2$, and so forth. A detailed optimization was performed for the sets with total $N = 1400$ and $N = 1600$. Quadruple precision was not sufficient at these $N$ and we used the multiprecision version of the program with 40 significant decimal digits. Further calculations with $N = 1800$–$2200$ were performed with 48 significant digits and only partial optimization of the parameters of the last layer (corresponding to the region where the logarithmic behavior is the most essential) was performed. Some optimization of the distribution of $n_i$ be-

TABLE V. Other examples of three-body calculations. ($L$ is the total angular momentum and $v$ the vibrational quantum number.)

| System | | $E$ |
|---|---|---|
| $e^- e^- e^+$ | This work | $-0.2620050702329801077(3)$ |
| | [18] | $-0.262005070232976$ |
| $\mathrm{He}(2^3P)$ | This work | $-2.13316419077928310(2)$ |
| | [19] | $-2.13316419077927(1)$ |
| $4\mathrm{He}+p$ $(L=35, v=0)$ | This work | $-2.98402095449725(1)$ |
| | [20] | $-2.98402094$ |
| $\mathrm{H}_2^+$ $(L=0, v=19)$ | This work | $-0.4997312306$ |
| | [21] | $-0.49973123063$ |

tween the layers ($N = n_1 + n_2 + n_3 + n_4$) was carried out as well.

As can be seen from Tables I and II, the present result extends the accuracy of the nonrelativistic ground-state energy for the helium atom by as many as three decimal digits.

Our second case is the hydrogen molecular ion ground state, which represent another limit of mass distribution of constituents with one light and two heavy particles. For this case it is especially essential that we introduce complex exponents, because it is the most natural way to fit the oscillatory behavior of the vibrational motion in the wave function. In this case (see Table III) again 40 decimal digits were used for $N = 1400 - 1800$ and 48 decimal digits for large $N$ to provide numerical stability of the calculations. Table IV demonstrates the progress in obtaining the variational nonrelativistic energy for this state. The accuracy is extended by as many as four additional digits.

In Table V other examples are summarized. The negative positronium ion demonstrates the limit of three particles of equal masses. The second and third cases are applications of the method to states with nonzero angular momentum. The last example in this table is of special interest. That is the last vibrational state in the series of $S$ states of the hydrogen molecular cation, and this calculation is the first variational confirmation of the existence of this state to our knowledge [the binding energy corresponding to the cited value is 0.744 21(2) cm$^{-1}$]. The accuracy of the artificial channel scattering

method [21] is presumably better; however, wave functions are not forthcoming with this method which makes difficult the calculation of physical properties of the state other than energy.

One may say that this high accuracy is redundant and has no physical meaning. But obviously it shows the power of modern computers and their ability to solve the quantum three-body problem to any required accuracy. On the other hand, uncertainty in the variational wave function is approximately as much as the square root of the uncertainty in the variational energy and is about $10^{-9} - 10^{-10}$. This accuracy does not look redundant. These results prove that the nonrelativistic bound-state three-body problem is now satisfactorily solved and the main efforts should be addressed to relativistic and QED effects.

The other advantage of the method is the simplicity of the basis functions which allows for analytic evaluation of the relativistic matrix elements of the Breit Hamiltonian (see, for example, Ref. [22]). It is possible as well to evaluate analytically the vacuum polarization term (Uehling potential) [23] and to build up an effective numerical scheme for one-loop self-energy corrections [24]. These features make the variational method considered a very powerful universal tool for studying the three-body problem.

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