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A Note on the Implementation of Variational Procedures Involving Green's Operators

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The numerical implementation of a minimum energy principle for atoms and molecules involving integral operators is discussed. It is demonstrated that the use of unscaled trial functions may be as convenient computationally as the earlier procedures involving scaled trial functions and that the revised prescription has advantages, mainly in ease of interpretation and comparison of results. By way of illustration, some earlier calculations on the H_2^+ ion are re-considered and compared.

Key words: Unscaled variational calculations – Green's functions

1. Introduction

In recent years considerable attention has been given to the proposal by Hall [1] to reformulate the Schrödinger equation

$$(T+V)\psi = E\psi \tag{1}$$

as an integral equation in the form

$$G_k V\psi = \mu\psi \tag{2}$$

where the integral operator G_k is defined by

$$G_k = (-\tfrac{1}{2}k^2 - T)^{-1} \tag{3}$$

with the eigenvalue E written as

$$E = -\tfrac{1}{2}k^2 \tag{4}$$

The eigenvalue parameter μ introduced in Eq. (2) is such that the physically significant eigenfunctions correspond to $\mu = 1$, the values of k being suitably adjusted. The process is seen to be equivalent to replacing the potential by $\mu^{-1}V$ for Coulombic systems, the parameter μ being regarded as a scaling factor, as in the work of Löwdin [2].

The integral equation (2) is then solved variationally by finding the stationary values of the functional

$$\mu[\phi] = (\phi V, G_k V\phi)/(\phi V, \phi) \tag{5}$$

corresponding to the trial function $\phi(r)$ and subject to the condition

$$\mu = 1 \tag{6}$$

The resulting value of k used in Eq. (4) then provides an upper bound for the ground state energy E_0. The application of this procedure to atomic and molecular systems has been considered by Hall, Hyslop and Rees [3, 4] who discuss in detail some of the scaling techniques which may be utilized in practice, the latter point also being discussed by Robinson and Epstein [5].

In many applications [6-9] it was found to be advantageous to use the parameter k itself as scaling factor. Hence, on utilizing trial functions of the form

$$\phi(\mathrm{r}) = \omega(kr) \tag{7}$$

the functional (5), subject to condition (6), takes the *direct* form

$$k[\omega] = (\omega V, G_1 V\omega)/(\omega V, \omega) \tag{8}$$

where the scaled Green's operator G_1 is given by

$$G_1 = (-\tfrac{1}{2} - T)^{-1} \tag{9}$$

All quantities in Eq. (8) are expressed in terms of the scaled variables $x = kr$. The advantage of this formulation is that k may be optimized (maximized) *directly* with respect to the trial function ω, using standard direct search techniques, the solution of the non-linear equation for k arising from (5) and (6) having been avoided.

However, there are certain difficulties, usually of interpretation, which arise in the practical use of the scaled trial functions (7). For instance, in molecular systems where the internuclear distances R are regarded as parameters, it is necessary to pre-set the *scaled* values kR, so that the actual value of R is not known until the approximate energy has been calculated. Again, in self-consistent field calculations involving scaled trial functions, Hyslop and Rees [9] have noted that the interpretation of such quantities as scaled interaction energies requires care when variation-iteration techniques are employed. More generally, the coupling of the self-consistent field equations means that the relation determining any given orbital incorporates the scaling factors of the other orbitals and these must therefore be determined iteratively at each stage of the calculation. This has proved to be computationally inconvenient in applications to three and four electron systems which are being currently investigated.

Consequently, in the present paper, an alternative computational scheme based on the unscaled Eqs. (5) and (6) is presented. Additional non-linear parameters may be incorporated in the trial functions to provide the flexibility previously obtained from scaling and optimization.

2. Formulation of the Unscaled Equations and Optimization

The trial function ϕ is expressed as the linear combination

$$\phi = \sum_{i=1}^{n} \gamma_i \phi_i \tag{10}$$

and additional non-linear parameters $c_1, c_2, \ldots c_m$ are included in the basis set $\{\phi_i\}$. The variational parameters are denoted collectively by the column vector

$$\boldsymbol{\alpha} = [\gamma_1, \gamma_2, \ldots \gamma_n, c_1, c_2, \ldots c_m]' \tag{11}$$

whose components are $\alpha_j, j = 1, 2, \ldots (n + m)$.

The functional (5) may now be expressed as

$$\mu(\boldsymbol{\alpha}, k) \tag{12}$$

and the conditions that μ should be stationary and simultaneously equal to unity give rise to the simultaneous equations

$$\mu = 1 \tag{13}$$

$$\partial\mu/\partial\alpha_j = 0 \qquad j = 1, 2, \ldots (n + m) \tag{14}$$

for the unknowns $\boldsymbol{\alpha}$ and k.

Eq. (13) may be expressed in matrix form as

$$\mu = (\gamma^\dagger G\gamma)/(\gamma^\dagger V\gamma) = 1 \tag{15}$$

where the column vector γ is given by

$$\gamma = [\gamma_1, \gamma_2, \ldots \gamma_n]' \tag{16}$$

and the elements of the matrices G and V are defined by

$$G_{ij} = (\phi_i V, G_k V\phi_j) \tag{17}$$

and

$$V_{ij} = (\phi_i V, \phi_j) \tag{18}$$

Optimization with respect to the linear parameters γ implies that

$$(G - \mu V)\gamma = 0 \tag{19}$$

The resulting secular equation effectively producing a non-linear equation for k and then yielding the corresponding eigenvectors γ.

Subsequent optimization with respect to each of the components c_λ of the vector

$$\mathrm{c} = [c_1, c_2, \ldots c_m]' \tag{20}$$

produces the set of non-linear equations

$$\xi^{(\lambda)} = (\gamma^\dagger F^{(\lambda)}\gamma)/(\gamma^\dagger U^{(\lambda)}\gamma) = 1 \qquad (\lambda = 1, 2, \ldots m) \tag{21}$$

the matrix elements being given by

$$F_{ij}^{(\lambda)} = (\partial\phi_i/\partial c_\lambda V, G_k V\phi_j) \tag{22}$$

and

$$U_{ij}^{(\lambda)} = (\partial\phi_i/\partial c_\lambda V, \phi_j) \tag{23}$$

In practice, it is seen that $(m + 1)$ non-linear equations are obtained for the unknowns c and k and solution by iteration is proposed. At the rth stage of the iteration, $(m + 1)$ input values $\mathrm{c}^{(r)}$ and $k^{(r)}$ are required. The matrix eigenvalue equation is then solved in the usual way, the largest positive eigenvalue $\mu^{(r)}$ being computed together with the corresponding eigenvector $\gamma^{(r)}$. These results are then used in Eqs. (21) to produce values for $\xi^{(\lambda)}$ which, in conjunction with the current value $\mu^{(r)}$ of μ, provide the $(m + 1)$ function values required by the algorithm for the solution of the non-linear equations.

This numerical scheme, involving an $(n \times n)$ matrix eigenvalue problem coupled with the solution of $(m + 1)$ non-linear equations, has been found to be highly competitive with the scaled approach which would involve the eigenvalue problem and an m-dimensional optimization at the second stage.

It is essential to use routines which minimize the number of function evaluations required, since most of the computational effort is needed for the evaluation of the matrix elements, particularly those involving the Green's operator G_k. The method of Peckham [10] has been found to be extremely efficient in this respect for the solution of the non-linear Eqs. (15) and (21). The extra time taken per iteration compared with more standard procedures, such as that of Powell [11], is unimportant relative to the number of function evaluations saved.

3. Numerical Applications and Discussion

A number of calculations have been carried out recently [7, 8] on the hydrogen molecular ion. In each case, these have been based on the scaled functional of Eq. (8) and it is therefore of interest to compare the procedures adopted there with the present general approach with unscaled trial functions.

The electronic potential energy is given by

$$V(r) = -(r_a^{-1} + r_b^{-1}) \tag{24}$$

where r_a and r_b are the distances between the electron and the nuclei A and B whose separation is R. Initially two simple trial functions are considered, namely:

1) $\phi = \phi_1 = \exp(-cu)$ (25)

2) $\phi = \phi_1 + \gamma\phi_2 = (1 + \gamma v^2) \exp(-cu)$ (26)

where the usual two-centre elliptic coordinates u and v have been used with

$$u = (r_a + r_b)/R, \qquad v = (r_a - r_b)/R \tag{27}$$

The first of these, ϕ_1, is the simple united atom approximation utilized in [7] and is included for comparison purposes with the earlier work. The second trial function is the classical one suggested by James [12] which was also discussed by Dalgarno and Poots [13] in the context of the Rayleigh-Ritz variational formulation.

The elements of the matrices V and U of Sect. 2 are easily evaluated analytically using the elliptic coordinates (27). For the matrices G and F the method suggested by Blakemore *et al.* [7] is adopted. Fourier transforms are used to reduce the integrals to triple quadratures which are then completed numerically using the suggested polar grids. The matrix elements are most efficiently evaluated simultaneously using the same grid points in each case. The iterative numerical scheme outlined in Sect. 2 was then utilized to compute the eigenvalues and it was found that extremely rapid convergence was achieved, the procedure being highly competitive with the scaled prescription of the earlier work. Excellent initial values for c and k are, of course, available here by interpolation from the tabulated results of Ref. [7]. In the case of the trial function ϕ_1, results which are identical with the scaled calculations are obtained when the same R values are used, as was verified by taking the values quoted in [7]. However, in the present case, the R values may be pre-set as parameters which is considerably more convenient for tabulation purposes.

Table 1. Electronic energies, $-E$, at internuclear separation R

R	1[a]	2[b]	3[c]	4[d]	5[e]	Exact
0.0	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000
0.1	1.9782	1.9782	1.9782	1.9782	1.9782	1.9782
0.5	1.7337	1.7346	1.7347	1.7349	1.7343	1.7350
1.0	1.4456	1.4496	1.4515	1.4517	1.4514	1.4518
1.5	1.2353	1.2431	1.2487	1.2489	1.2487	1.2490
2.0	1.0798	1.0912	1.1024	1.1026	1.1024	1.1026
2.5	0.9607	0.9754	0.9935	0.9937	0.9936	0.9938
3.0	0.8665	0.8841	0.9103	0.9107	0.9107	0.9109
3.5	0.7902	0.8101	0.8455	0.8462	0.8464	0.8466
5.0	0.6280	0.6530	0.7193	0.7224	0.7242	0.7244
7.0	0.4963	0.5250	0.6294	0.6395	0.6484	0.6485
10.0	0.3802	0.4108	0.5481	0.5716	0.6006	0.6006

[a] Rayleigh-Ritz functional (28), trial function (25).
[b] Green's Operator functional (5), trial function (25).
[c] Rayleigh-Ritz functional (28), trial function (26).
[d] Green's Operator functional (5), trial function (26).
[e] Green's Operator functional (5), trial function (29).

The results for both trial functions (25) and (26) are presented in Table 1 where the exact electronic energies obtained by Wind [14] are also quoted. For comparison purposes the approximate energies generated by the classical Rayleigh-Ritz functional

$$E = (\phi, (T + V)\phi)/(\phi, \phi) \tag{28}$$

are shown for these trial functions. The advantage of the unscaled approach now becomes apparent in that direct comparison between the various sets of results may now be made at the same values of the internuclear separation. In previous scaled calculations, because of the differing scaling factors, such direct comparisons were not possible, since the *scaled* values were pre-set in each case. It will be seen that, in all cases, the upper bounds obtained by the Green's function approach are superior to the Rayleigh-Ritz results, the compensating disadvantage being, of course, the increased complexity of the required integrations. The main reason for this superiority is that the trial functions are operated on by the Green's integral operator essentially before being employed in the corresponding variational functional. This produces a smoothing effect and also implies that a considerable amount of information regarding the physical nature of the system has been effectively built into the wave function, by means of the associated Green's function. The resulting superiority of the Green's function bounds has been demonstrated theoretically in Refs. [3] and [4].

Note also that neither of the united atom trial functions (25) nor (26) will produce the correct limiting energies in the separated atoms limit as $R \to \infty$, although they are exact as $R \to 0$. For this reason, it was decided to apply also the separated atom trial function of Ref. [8]. In this case, the problem of numerical integration was obviated by using potential weighted trial functions of the form ϕV, as detailed in the earlier work. To provide a more stringent test of the present numerical procedure the most complicated trial function of Ref. [8] was adopted. This involved a trial function of the form

$$\phi V = \sum_{i=1}^{6} \gamma_i \Phi_i \tag{29}$$

the orbitals being expressed as

$$\Phi_i = \phi_a(n_i, l_l, m_i, c_i) + \phi_b(n_i, l_i, m_i, c_i) \tag{30}$$

the subscripts a and b denoting that the orbitals are centred on nuclei A and B respectively. Modified Slater functions are used for ϕ_a and ϕ_b as outlined in Ref. [8] and, in this particular case, the six orbitals corresponding to the $1s$, $2s$, $2p$, $3s$, $3p$ and $3d$ states (with $m_i = 0$ in each case) are included. The results of this calculation are also presented in the Table and it is noted once more that this procedure for solving the unscaled equations compares favourably with the earlier scaled prescription as well as producing a more convenient tabulation. The approximate eigenvalues are in good agreement with the exact energies over the complete range of R.

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