

## Orthogonality constrained general variational calculation of excited state wavefunctions and energies: A new strategy

PRIYATOSH DUTTA and S P BHATTACHARYYA

Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India

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**Abstract.** A viable strategy is developed for the general variational calculation of excited state wavefunctions which are constrained to remain *orthogonal* to all the lower-lying states of the same *symmetry*. A key element of the strategy is to employ the penalised functional procedure for enforcing the relevant orthogonality constraints and the method of steepest descent to locate the constrained minima with respect to all variables, linear as well as nonlinear. The workability of the algorithm is tested by applying the technique for the optimization of nonlinear parameters in trial functions for the 2s state of H atom and singlet 1s2s states of helium atom and some isoelectronic ions.

**Keywords.** Constrained variation; variational calculation of excited states; orthogonality constrained variation; penalised functional method.

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### 1. Introduction

The Ritz variational principle asserts that for any arbitrary trial function ( $\tilde{\psi}$ ) satisfying the appropriate boundary conditions, the energy expectation value  $\tilde{E}$  is an upper bound to the exact ground state energy ( $E_0$ ) of the system (Epstein 1974) described by the hamiltonian  $\hat{H}$  (viz.)

$$\tilde{E} = \langle \tilde{\psi} | \hat{H} | \tilde{\psi} \rangle / \langle \tilde{\psi} | \tilde{\psi} \rangle \geq E_0.$$

The upper boundedness of  $\tilde{E}$  is no longer valid for variationally computed excited state energies unless the trial function ( $\tilde{\psi}$ ) is constrained to be orthogonal to all the lower-lying states of the same symmetry. However, if the trial space is linear, the Hylleraas Undheim Macdonald (HUM) theorem guarantees the upper boundedness of the computed energies (Hylleraas and Undheim 1930; Macdonald 1933; Epstein 1974). The required linearity of the trial space can be easily satisfied by taking the trial function in the form of a linear combination of a linearly independent set of basis functions and varying only the linear parameters in the trial function. The basis functions may contain nonlinear parameters which are held fixed during the variation. This restriction on the variational freedom affects the flexibility of the trial function, for it is well known that several linear parameters are generally required to mimic the effects of variation of a single nonlinear parameter. It would be desirable therefore to have a method which permits one to perform a general variational calculation on an excited state without sacrificing the orthogonality of the computed excited state

wavefunctions to the lower-lying states of the same symmetry. If the lower-lying exact eigenstates of  $\hat{H}$  are known, orthogonality constrained variation ensures strict upperboundedness of the computed excited state energies in spite of variations of the non-linear parameters. The same is not true when only approximate lower state functions are available. Nevertheless, one can try to optimize the non-linear variational parameters for a manifold of states (ground and several excited states of the same symmetry) at the same level of sophistication or approximation by resorting to the use of orthogonality constrained variation method. This would amount to the optimization of the 'Ritz basis vectors' for a manifold of states which could enhance the convergence of a subsequent linear variational calculation within the same manifold.

In quantum theoretical calculation of atomic and molecular electronic structure, the ground and lowest electronic state of each symmetry is commonly described by approximate wavefunctions determined variationally by applying the SCF method. The result of an SCF calculation provides the 'parent configuration' which is usually supplemented by invoking the linear variation method (cf HUM theorem) in the manifold of electronic states generated by the SCF orbitals (The so called CI method). The convergence of CI expansion is generally very slow. The same two step hierarchy (viz. SCF + CI) can, in principle, be adopted to describe an arbitrary excited state as well. But the scheme in this case is much less well defined. This is because the 'parent excited state configuration' may not be amenable to SCF calculation. CI expansion around a 'non-parent configuration' is rather inefficient.

The MC-SCF method on the other hand invokes a nonlinear variational strategy wherein the CI expansion coefficients and orbital forms are both optimized. The nonlinear orbital optimization step is, however, plagued by problems originating from variational collapse and manifested in 'root-flipping' (Docken and Hinze 1972; Chang and Schwarz 1977; Werner and Meyer 1981). The search for alternative techniques which avoid the problem of variational collapse while performing nonlinear variational calculations on excited states, although cursory, can be found in literature. These invariably involve either the application of the Hylleraas perturbation variation method (Sinanoglu 1961; Miller 1966; Chang 1980) or the use of orthogonality constrained variation method. Although the basic philosophy underlying the latter method has been well known, practical computational difficulties have led researchers in the field to consider the method as more or less untractable (Chang 1980). Nevertheless, few attempts in this direction can be found in the literature (Weber and Handy 1969; Wang et al 1973; Hendekovic 1983). It appears that these methods have never been numerically evaluated or pursued seriously. Our purpose in this communication has been to explore a new strategy for tackling the orthogonality constrained variational method – a strategy that is computationally easy to handle and leads to a tractable numerical recipe. In what follows we first describe the algorithm. The workability of the algorithm is then tested by applying the method to some model problems. Possible avenues of improving the algorithm are suggested.

## 2. The method

Let  $\phi_1, \phi_2, \phi_3 \dots \phi_{n-1}$  be the first  $(n-1)$  eigenstates (exact or approximate) of a given hamiltonian  $\hat{H}$ . Let the corresponding energies be  $\epsilon_1, \epsilon_2, \epsilon_3, \dots, \epsilon_{n-1}$ .  $\tilde{\psi}$  is the trial

wavefunction for the  $n$ th eigenstate of  $\hat{H}$  which is constrained to remain orthogonal to  $\phi_1, \phi_2, \dots, \phi_{n-1}$  during variation. The constraint conditions are therefore

$$\langle \hat{\psi} | \phi_k \rangle = \langle \phi_k | \hat{\psi} \rangle = 0 \text{ for } k = 1, 2, 3, n-1. \quad (1)$$

Some of the conditions in (1) may be automatically satisfied for reasons of symmetry (eg  $\hat{\psi}, \phi_k$  belong to two different irreducible representations of the symmetry group to which  $\hat{H}$  belongs). For the sake of generality we assume that all the constraint conditions in (1) are non-trivial. Having explicated the constraint conditions we may now define an  $(n-1)$  fold constrained energy functional as follows (Fiacco and McCormick 1968; Morrison 1969; Fiacco 1970; Das and Bhattacharyya 1985, 1986, 1987).

$$\tilde{\mathcal{F}}_c(\xi) = \{\varepsilon_c(\xi) - \varepsilon_1\}^2 + \sum_{k=1}^{n-1} \lambda_k g_k(\langle \tilde{\psi} | \phi_k \rangle). \quad (2)$$

In (2)  $\varepsilon_1$  is a lower bound to the constrained energy  $\tilde{\varepsilon}(\xi)$ . The  $g_k(\langle \tilde{\psi} | \phi_k \rangle)$  s are appropriate penalty functions such that,

$$g_k(\langle \tilde{\psi} | \phi_k \rangle) = 0 \quad (k = 1, 2, \dots, n-1),$$

only when all the constraints in (1) are satisfied. If the constraints are violated,  $g_k$ s rise sharply and  $g_k(\langle \tilde{\psi} | \phi_k \rangle) > 0$  if the  $k$ th constraint is violated. A variety of functional forms can be chosen for  $g_k$ , the simplest of which is

$$g_k(\langle \tilde{\psi} | \phi_k \rangle) = [\langle \tilde{\psi} | \phi_k \rangle]^2$$

$\lambda_k$ s are penalty weight factors of appropriate magnitudes and dimensions. The minimum of  $\tilde{\varepsilon}_c(\xi)$  then corresponds to a set of values for  $(\xi) = (\xi_c)$  such that

$$\langle \tilde{\psi}(\xi_c) | \phi_k \rangle = 0 \quad \text{for } k = 1, 2, \dots, n-1 \text{ and } \varepsilon(\xi) = \varepsilon_1 = \varepsilon_c(\xi).$$

The constrained variational parameters are therefore determined by the stationary condition of  $\mathcal{F}(\xi)$  for arbitrary variation  $\delta\xi$  in  $\xi$  (viz).

$$\delta\mathcal{F}(\xi) = 0, \quad \text{which immediately leads to}$$

$$2[\{\varepsilon(\xi) - \varepsilon_1\}](\partial\varepsilon/\partial\xi)\delta\xi + 2\sum_{k=1}^{n-1} \lambda_k [g_k(\langle \tilde{\psi} | \phi_k \rangle)(\partial g_k/\partial\xi)]\delta\xi = 0$$

since  $\delta\xi$  is arbitrary, we have, from the preceding equation

$$2[\varepsilon(\xi) - \varepsilon_1](\partial\varepsilon/\partial\xi) + 2\sum_{k=1}^{n-1} \lambda_k [g_k(\langle \tilde{\psi} | \phi_k \rangle)(\partial g_k/\partial\xi)] = 0. \quad (3)$$

Instead of trying to solve (3) for  $\xi = \xi_c$  directly, a more viable strategy would be to seek the minimum of  $\mathcal{F}(\xi)$  by adopting a direct functional minimization procedure. One way to do this is to invoke the method of steepest descent (SD) for the minimization of  $\mathcal{F}(\xi)$ . Since it is, in any case, going to be an iterative process, we must have a well defined scheme of estimating (or updating) the lower bound  $\varepsilon_1$  to  $\varepsilon(\xi)$  at any specific stage of the iterative process. A convenient way of doing this is to adopt the following approach (Morrison 1969). Let  $\varepsilon_1^i$  be a lower bound to the

constrained energy  $\varepsilon^i$  at the  $i$ th stage of the iterative process. Let the constrained functional have the value  $S_i$  at this stage. The lower bound for the next cycle is then updated by taking

$$\varepsilon_1^{i+1} = \varepsilon_1^i + \eta(S_i)^{1/2} \quad (4)$$

where

$$S_i = \mathcal{F}_c^i(\xi) = (\varepsilon_1^i - \varepsilon^i)^2 + \sum_k g_k(\langle \tilde{\psi}_i | \phi_k \rangle) \quad (5)$$

$\eta$  is a damping parameter which should lie in the range  $0 < \eta \leq 1$ . An appropriate choice of  $\eta$  is very important for the achievement of smooth convergence (see later). When an appropriate value of  $\eta$  has been chosen, we may try to locate the constrained minimum in the following way.

Let  $\xi_1^0, \xi_2^0, \dots, \xi_n^0$  be the starting set of parameters in the trial wave function ( $\tilde{\psi}$ ). Taylor's expansion of  $\mathcal{F}(\xi_k)$  around  $\xi_k^0$  gives us

$$\mathcal{F}(\xi_k) = \mathcal{F}(\xi_k^0) + (\partial \mathcal{F} / \partial \xi_k)_{\xi_k = \xi_k^0} \delta \xi_k + \dots$$

If one sets  $\delta \xi_k = -\lambda (\partial \mathcal{F} / \partial \xi_k)_{\xi_k = \xi_k^0}$  where  $\lambda$  is an appropriately small positive scalar,  $\mathcal{F}(\xi_k) < \mathcal{F}(\xi_k^0)$  is ensured. Although a sufficiently small  $\lambda$  will ensure minimization of  $\mathcal{F}(\xi_k)$ , the best or steepest rate of descent can be achieved by further minimizing  $\mathcal{F}(\xi_k)$  with respect to the step length parameter  $\lambda$  (Mcweeny 1960, 1968). This, however, requires an explicit knowledge of the second derivative of  $\mathcal{F}(\xi)$  with respect to  $\xi$ .

### 3. Results and discussion

The workability of the algorithm is amply demonstrated by the following numerical examples. The examples belong to two distinct categories described earlier.

#### 3.1 Where the exact lower state wavefunctions of the same symmetry are known

The example under this category belongs to the class of problems where the exact wavefunctions for the  $(n-1)$  lower lying states are available. The hydrogen atom is a case in point. The exact ground state of H atom is given by

$$\psi_0(r) = \frac{1}{\sqrt{\pi}} \exp(-r).$$

Let the trial wavefunction for the  $2s$  state be chosen in the form

$$\tilde{\psi}_{2s}(r) = \tilde{\psi}_1(r) = N(1 + \beta r/2) \exp(-\alpha r/2).$$

The form chosen for  $\tilde{\psi}_1$  has been deliberately made to make it coincide with that of the exact  $\psi_{2s}$ ; for our basic purpose is to demonstrate the ability of our algorithm to prevent variational collapse even in the worst case and optimize the nonlinear parameters simultaneously.

If one tries to minimize the energy  $E_{2s}(\alpha, \beta) = \langle \tilde{\psi}_1 | H | \tilde{\psi}_1 \rangle / \langle \tilde{\psi}_1 | \tilde{\psi}_1 \rangle$  directly, without enforcing the constraint  $\langle \tilde{\psi}_1 | \psi_0 \rangle = \langle \psi_0 | \tilde{\psi}_1 \rangle = 0$ , one anticipates variational collapse to the ground state to occur whichever set of  $\alpha, \beta$  one starts with as  $\tilde{\psi}_1(r) = \psi_0(r)$  for

**Table 1.** Comparison of the results obtained by applying the unconstrained and an orthogonality constrained variational procedure to the 2s state of H atom ( $\tilde{\psi}_{2s} = \exp(-ar/2)(1 + \beta r/2)$ ); convergence criterion are the same in each case).

Method	Starting values of variational parameters		Optimized values* of variational parameters $\alpha'/\beta'$	Starting values of energy ( $E_0$ ) and overlap ( $S_0$ ) with the ground state $E_0(\text{a.u.})/S_0$	Final values of energy ( $E$ ) and overlap ( $S$ ) with the ground state $E(\text{a.u.})/S$
	$\alpha_0$	$\beta_0$			
UVM	0.75	-0.25	0.99487/ $1.0867 \times 10^{-16}$		-0.49566/ 0.99406
OCVM	0.75	-0.25	0.5031/ -0.5093	-0.46875/ 0.9596	-0.12494/ $-0.970 \times 10^{-11}$

$$\alpha' = \alpha/2, \beta' = \beta/2$$

$\alpha=2, \beta=0$ . This is what happens when we attempt an unconstrained minimization of  $\mathcal{F}(\xi)$  in our model which amounts to setting all the  $\lambda_k$ s equal to zero in (2). Table 1 displays the initial values of  $\alpha, \beta$  as well as the initial energy and overlap of trial  $\tilde{\psi}_1$  with the exact ground state wavefunction  $\psi_0$  and the corresponding quantities at convergence. The collapse is evident. The corresponding quantities for the constrained variational optimization of  $E_{2s}(\alpha, \beta)$  are also reported in the same table for comparison. It is clear that our orthogonality constrained model for the variational determination of non-linear (as well as linear) parameters characterizing the excited state wavefunction prevents variational collapse completely and produces energies which are upperbound to the exact energies of the corresponding excited states, when exact lower state wavefunctions are known. In the present case, we could recover the exact energy of the 2s state since the analytical form of the trial 2s state wavefunction coincided with the known one.

### 3.2 Constrained minimization when only approximate lower state wavefunctions are known

This is the situation one normally expects to encounter. The questions that naturally arise are (i) whether the method proposed can operate with equal facility in a case where exact lower state wavefunctions are not available to start with; (ii) whether the computed energies retain their upperbound character; (iii) what can be done to improve the quality of the results. To investigate these points we take up the singlet (1s2s) states of helium or helium-like atoms as examples. Two different types of basis sets are employed. In the first, we approximate the ground state by the Hylleraas-Eckert wave function ( $\tilde{\psi}_0$ ) (Eckert 1930) which has two adjustable non-linear parameters  $\alpha_0$  and  $\beta_0$

$$\tilde{\psi}_0(r_1, r_2) = N_0 \{ \exp[-(\alpha_0 r_1 + \beta_0 r_2)] + \exp[-(\beta_0 r_1 + \alpha_0 r_2)] \}.$$

The approximate trial wavefunction (space part) for the singlet (1s2s) state ( $\tilde{\psi}_1$ ) is also chosen in the same form:

$$\tilde{\psi}_1(r_1, r_2) = N_1 [ \mathcal{U}_{1s}(\alpha', r_1) \mathcal{V}_{2s}(\beta', r_2) + \mathcal{U}_{1s}(\beta', r_1) \mathcal{V}_{2s}(\alpha', r_2) ]$$

where

$$\mathcal{U}_{1s}(\alpha', r) = N_{1s} \exp(-\alpha' r) \text{ and}$$

$$\mathcal{V}_{2s}(\beta', r) = N_{2s}(1 + \beta' r/2) \exp(-\beta' r/2)$$

$N_0$ ,  $N_1$ ,  $N_{1s}$  and  $N_{2s}$  are the corresponding normalization constants. In our orthogonality constrained variational model the functional (penalised) to be minimized is

$$\mathcal{F}(\alpha', \beta', \alpha^0, \beta^0) = \{\varepsilon(\alpha', \beta') - \varepsilon_1\}^2 + \lambda[S(\alpha', \beta', \alpha^0, \beta^0)]^2$$

where

$$S(\alpha', \beta', \alpha^0, \beta^0) = \langle \tilde{\psi}_0(r_1, r_2) | \tilde{\psi}_1(r_1, r_2) \rangle.$$

The minimization is to be done with respect to  $\alpha'$  and  $\beta'$ , while  $\alpha^0$  and  $\beta^0$  are held constant. Table 2 reports the orthogonality constrained optimal values of  $\alpha'$ ,  $\beta'$  the computed energy and overlap with the ground state wavefunction ( $\tilde{\psi}_0$ ). It is clear that  $\tilde{\psi}_1$  is orthogonal to  $\tilde{\psi}_0$  and  $\tilde{E}'_1$  is upperbound to the exact energy (Sharma and Coulson 1961). The unconstrained variational results are also included in table 2 for comparison. The computed energy  $\tilde{E}_1$  is slightly lower than the constrained energy ( $\tilde{E}'_1$ ) although no sign of variational collapse is evident in  $\tilde{E}_1$  (unconstrained). In fact the form of the trial wavefunction ( $\tilde{\psi}_1$ ) has been so chosen as to prevent the possibility of a complete collapse onto the ground state. It is however, clear from table 2 that  $\tilde{\psi}_1$  (unconstrained) is not orthogonal to  $\tilde{\psi}_0$  ( $S \approx 10^{-3}$ ). Thus our method is capable of generating a manifold of completely optimized and rigorously orthonormal set of basis vectors of a particular symmetry. One can use these vectors for further linear variational calculations which should lead to faster convergence as no a priori structure has been assumed for the Ritz-basis vectors. They have been fully optimized for the particular manifold consistent with the orthogonality requirement.

Table 3 presents another set of results for the singlet 1s2s states of a few members of the He isoelectronic sequence with a different choice of the basis functions. The

**Table 2.** Comparison of the results obtained by applying the unconstrained and an orthogonality constrained variational procedure to the singlet 1s2s state of helium atom ( ${}^1\tilde{\psi}_{1s2s}$  and  $\tilde{\psi}_{1s2s}$  are approximated by the corresponding Hylleeraas-Eckert function).\*

Method	Starting values of variational parameters		Optimized values of variational parameters $\alpha_1/\beta_1$	Starting values of energy ( $E_a$ ) and overlap ( $S_0$ )	Final values of energy ( $E$ ) and overlap ( $S$ )
	$\alpha_1^0$	$\beta_1^0$		$E_0(\text{a.u.})/S_0$	
UVM	2.15	1.20	1.83649/ 1.50295		-2.05879/ -0.00129
OCVM	2.15	1.20	1.84593/ 1.49522	-2.01796 $4.74 \times 10^{-2}$	-2.05859/ $-1.94 \times 10^{-12}$
Exact results (Sharma and Coulson)					-2.147294

\*Eckert 1932

**Table 3.** Comparison of the results obtained by applying the unconstrained and an orthogonality constrained variational procedure to the singlet  $1s2s$  states of helium atom and some isoelectronic ions.

Z	OCV Energy of singlet $1s2s$ state (a.u)	Overlap with $\psi_0$	Exact <sup>a</sup> energy (singlet $1s2s$ ) (a.u)	Exact <sup>b</sup> energy (ground state) (a.u)	Unconstrained energy (singlet $1s2s$ ) (a.u)
2	-2.010336	$3.6 \times 10^{-5}$	-2.14729	-2.9037	-2.80827
3	-4.318752	$2.6 \times 10^{-5}$	-5.04115	-7.2799	-7.07201
4	-6.503459	$3.2 \times 10^{-5}$	-9.18466	-13.6555	-13.28465
5	-10.21153	$4.5 \times 10^{-5}$	-14.57809	-22.0309	-21.44574
6	-13.11626	$4.24 \times 10^{-5}$	-21.22136	-32.4062	-31.55516

<sup>a</sup>Ref. Coulson and Sharma (1962)<sup>b</sup>Ref. Scherr and Knight (1963)

trial wavefunction (space part)  $\psi(r_1, r_2)$  is of the form

$$\tilde{\psi}(r_1, r_2) = N\{\phi_{1s}(r_1)\phi_{2s}(r_2)\}$$

where  $\phi$ 's are the appropriate ( $1s$  or  $2s$ ) single  $\xi$ -slater type of orbitals. The corresponding ground state ( $\tilde{\psi}_0$ ) is also represented by variationally determined antisymmetrized product of single  $\xi$ - $1s$  slater orbitals. The reason behind this particular choice of  $\tilde{\psi}(r_1, r_2)$  and  $\tilde{\psi}_0(r_1, r_2)$  lies in the possibility of a complete variational collapse of  $\tilde{\psi}(r_1, r_2)$  onto  $\tilde{\psi}_0(r_1, r_2)$  during the optimization of  $\xi$ -parameters. This could happen since  $\phi_{2s}(r_1)$  is nodeless and has a non-zero overlap with  $\phi_{1s}(r_1)$ . Perusal of table 3 clearly shows that the constrained calculations on the singlet  $1s2s$  state successfully avoid variational collapse onto the ground state while the unconstrained variational calculations invariably lead to collapse of the  $1s2s$  wavefunction onto the ground state. We may say that these constrained wave functions represent the best possible single  $\xi$ -STO based wavefunctions for the singlet  $1s2s$  states consistent with the requirement of orthogonality with the corresponding approximate ground state. The computed energies are no doubt upper bounds to the exact energies. But they are a bit too high. This is not unexpected because of the very limited variational freedom enjoyed by the single- $\xi$  STO based wavefunction for the singlet  $1s2s$  state subject to the orthogonality constraint. A linear combination of such functions is required to improve the situation. We are exploring this possibility at present.

#### 4. General features of the algorithm

We have made a preliminary study of the convergence behaviour of our algorithm. Our experience so far has been that a smooth and monotonic convergence can be achieved by our algorithm in all cases if  $\eta$  in (4) is properly chosen. The only requirement on  $\eta$  is that it should be a small positive scalar. Irrespective of the starting point the orthogonality constrained variational determination of the excited state wavefunction proceeds smoothly and converges to the same point, showing its stability. The constrained (penalised) functional value also decreases monotonically as the required orthogonality condition is satisfied more and more strictly with the increase

in the number of steepest descent iterations. The rate of convergence is slow as is expected of the steepest descent procedure. We are exploring some avenues for convergence acceleration in the framework of the steepest descent based procedures (Bevington 1969). The slow convergence is more than compensated by the extreme simplicity of the algorithm. The algorithm does not lose its simplicity with an increase in the number of constraints. Although we have employed the steepest descent technique for minimizing the penalised functional, one can invoke any other suitable unconstrained minimization technique. The relative merits and demerits of these different techniques in the present context are under evaluation. The numerical stability of the algorithm is excellent since we have always been able to reach the same constrained minimum quite independent of the starting point. The algorithm is thus expected to be useful in a two step hierarchy where the Ritz basis vectors of a particular manifold of excited states are first optimized subject to the orthogonality constraint and then a further linear variation is performed within the same manifold. Our algorithm can be used, in principle, with the two step manifold energy minimization procedure suggested recently by Hendekovic (1982) essentially on the basis of max-min theorem (Gould 1966; Epstein 1974). However no numerical data on the performance of this method is available for comparison. The one-step method proposed by Weber and Handy (1969) which involves the application of Ritz variational principle to an appropriately projected hamiltonian  $\bar{H}$  is much more cumbersome. For the first excited state having the same symmetry as the ground state ( $\phi_0$ ) the projected hamiltonian is given by

$$\bar{H} = (1 - P)H(1 - P)$$

where

$$P = |\phi_0\rangle\langle\phi_0| + |H\phi_0\rangle\langle H\phi_0|$$

The method is hardly tractable in view of its requirement to calculate the matrix elements of  $H^2$  and  $H^3$ . Its generalization to handle higher than the first excited state of the same symmetry appears to be almost impossible. In comparison, our algorithm does not increase in complexity when one goes to higher excited states of a particular symmetry.

### 5. Scope of improvement of the algorithm

It may be noted that  $\tilde{\psi}_1$  (constrained) is orthogonal to  $\tilde{\psi}_0$ . But since  $\tilde{\psi}_0$  is not the exact ground state of  $H$ , the optimized  $\tilde{\psi}_1$  (constrained) is not necessarily decoupled with  $\tilde{\psi}_0$ . That essentially means,

$$\langle\tilde{\psi}_1|\tilde{\psi}_0\rangle = 0, \quad \text{but } \langle\tilde{\psi}_1|\hat{H}|\tilde{\psi}_0\rangle \neq 0.$$

An obvious way of improving our results will be to incorporate the decoupling condition as an additional constraint and replace the two-step strategy by a single step one. Unlike the method of Weber and Handy (1969) this will not require the calculation of matrix elements of  $\hat{H}^2$  or  $\hat{H}^3$ . On the other hand, this would certainly lead to a viable, if not better, alternative to the linear variational method (Wang *et al* 1973). Another area of improvement is in the choice of the penalty functions. We have so far used the simplest possible form of  $g_k\langle\tilde{\psi}|\phi_k\rangle$ . Better choice of  $g_k$  may



enhance the convergence rate achievable by the algorithm. Finally, we have used the simplest possible forms of trial functions for the excited states in our exploratory calculation and chosen the ground state accordingly. We can make systematic improvements in both and improve both the upperbounds. We will address ourselves to some of these aspects in a future communication (Datta and Bhattacharyya 1989).

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