Alternative Technique for the Constrained Variational Problem Based on an Asymptotic Projection Method: I. Basics

Vitaly N. Glushkov(✉), Nikitas I. Gidopoulos, and Stephen Wilson

Abstract An alternative approach to problems in quantum chemistry which can be written as an eigenvalue equation with orthogonality restrictions imposed on eigenvectors is reviewed. The basic tenets of a simply implemented asymptotic projection method for taking the necessary orthogonality constraints into account are presented. The eigenvalue equation for a modified operator is derived and the equivalence of the original and modified problem is rigorously demonstrated. The asymptotic projection method is compared with the conventional approach to constrained variational problems based on the elimination of off-diagonal Lagrange multipliers and with other methods. A general procedure for application of the method to excited state problems is demonstrated by means of calculations of excited state energies and excitation energies for the one-electron molecular systems, H_2^+ and H_3^{++}.

Keywords: eigenvalue problem, orthogonality constraints, excited state, basis set optimization

V.N. Glushkov
Department of Physics, National University, Dnepropetrovsk, 49050, per.Nauchny 13, Ukraine,
e-mail: v_n_glushkov@yahoo.com

N.I. Gidopoulos
ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon, OX11 0QX, England, UK,
e-mail: n.gidopoulos@rl.ac.uk

S. Wilson
Physical & Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, England;
Faculty of Mathematics, Physics and Informatics, Comenius University, 84215 Bratislava, Slovakia, e-mail: quantumsystems@gmail.com

1 Introduction

It is well known that many problems in physics and, in particular, in quantum chemistry, can be formulated as an eigenvalue problem for a self-conjugate operator H with some orthogonality constraints imposed on its eigenfunctions.

In practice, one of the most important approximations inherent in essentially all standard *ab initio* calculations is to replace the exact solution of an eigenvalue problem in an infinite-dimensional Hilbert space of states X by a solution in a finite-dimensional subspace $M = PX$ with the corresponding orthoprojector P, i.e. we are concerned with the eigenproblem:

$$P(H - E_i)P|\Phi_i\rangle = 0,$$
$$|\Phi_i\rangle = P|\Phi_i\rangle, \ i = 0, 1, \ldots, n \tag{1}$$

subject to the constraints

$$\langle u_s|\Phi_i\rangle = 0, \ s = 1, 2, \ldots, q < n. \tag{2}$$

It is should be noted that, in general, the constraint vectors $|u_s\rangle \in X$ are not completely contained in the subspace M and are *arbitrary* with respect to the operator *PHP*.

It is clear that such an approximation reduces the accuracy of calculations. Furthermore, a finite subspace which is optimal for the lowest eigenvalue, E_0, will not, in general, support an acceptable accuracy for the higher eigenvalues. It is, therefore, necessary to adjust the subspace to the eigenvalue(s) being studied, by, for example, rotating the subspace M in X in an optimal manner.

Variational methods, such as the Rayleigh-Ritz method, are well adapted to the approximate solution of eigenvalue problems. In this method the desired vectors are represented by a linear combination of a finite number of basis vectors $|\phi_k(\rho)\rangle$ which, in general, depend on variational parameters $\rho_a, (a = 1, 2, \ldots, r)$

$$|\Phi_i\rangle = \sum_{k=0}^{n} C_{ik}|\phi_k(\rho)\rangle = P|\Phi_i\rangle. \tag{3}$$

The eigenvalues are determined by finding minimum of the Rayleigh quotient, i.e. the functional

$$E(\Phi) = \langle\Phi|H|\Phi\rangle/\langle\Phi|\Phi\rangle, \ \Phi \in M, \tag{4}$$

For example, the lowest eigenvalue, E_0, for the problem defined by Eqs. (1) and (2) is given by

$$E_0 = E(\Phi_0) = \langle\Phi_0|H|\Phi_0\rangle = \min_{\Phi \in M} E(\Phi), \ \langle\Phi_0|\Phi_0\rangle = 1 \tag{5}$$

$$\langle u_s|\Phi\rangle = 0, \ s = 1, 2, \ldots, q < n. \tag{6}$$

In other words, we are dealing with a constrained minimization problem. *Equations (5) and (6) define the constrained variational problem.* An example of this problem

arises in calculations for excited states in which a basis set specifically designed for the ground state is used to calculate the ground state energy and a different basis set is used in the description of an excited state. There has been a growing interest in quantum chemical problems of this type in recent years (see e.g. the work of Sadlej [1], of Assfeld and Rivail [2], and of Surjan [3]). Conventional methods of constrained optimization (see, e.g. the well-known texts by Himmelblau [4] and by Gill and Murray [5], and references therein) have not proved effective in solving the complicated problems of quantum chemistry, especially when for example, nonlinear basis set parameters are varied.

In this study, we shall show how the problem defined by Eqs. (5) and (6) can be solved in a way which is simpler than the traditional approaches employed in quantum chemical calculations. We review an easily implemented technique termed the *asymptotic projection method*. This work was proposed in earlier work by one of us (VNG) [6–8] and developed further in Refs. [9–15]. The asymptotic projection method was shown to be a useful tool for solving a wide class of problems in quantum chemistry which can be cast in the form of an eigenvalue equation with constraints.

This paper is arranged as follows: in Sect. 2, an overview of the asymptotic projection method is given. We compare asymptotic projection with other approaches to the constrained variational problem, in particular, the method of elimination of off-diagonal Lagrange multipliers method and the projection operators technique. A general approach to excited state problems using the asymptotic projection method method is described in Sect. 3. In Sect. 4, the potential of the method is demonstrated by means of calculations for the excited state energies and excitation energies for the one-electron molecular systems, H_2^+ and H_3^{++}. Some concluding remarks are given in Sect. 5.

2 Overview of the Asymptotic Projection Method

We shall demonstrate that the asymptotic projection method is based on the properties of self-conjugate operators. It is general and applicable to any problem that can be cast in the form of an eigenvalue equation with some orthogonality constraints imposed on the eigenvectors.

2.1 The Basic Theorem of the Asymptotic Projection Method

For the sake of simplicity, we limit ourselves initially to problems involving one constraint vector $|u\rangle$. In this case, the constrained variational problem is to minimize the Rayleigh quotient (4) subject to constraint

$$\langle u|\Phi\rangle = 0. \tag{7}$$

We can identify three possible situations for the constrainted vector $|u\rangle$ with respect to a subspace M spanned by the finite basis set:

(i) $P|u\rangle = 0$, this is a trivial case. The minimization can be performed by well-established unconstrained optimization methods.

(ii) $P|u\rangle = |u\rangle$, the constraint vector lies completely within the subspace M.

(iii) $P|u\rangle \neq 0$, $P|u\rangle \neq |u\rangle$, then the constraint vector can be divided into two parts

$$|u\rangle = P|u\rangle + (I - P)|u\rangle \tag{8}$$

where the first term on the right-hand side lies completely within M and the second term lies in $M^{\perp}$, the orthogonal complement of M.

Here and in the following I is the identity operator.

Thus, we are only required to consider the case (ii), i.e., the constraint vector is $P|u\rangle$. Without loss of generality, we can take this constraint vector to be normalized $|\widetilde{u}\rangle = P|u\rangle / (\langle u|P|u\rangle)^{\frac{1}{2}}$, i.e. $\langle \widetilde{u}|\widetilde{u}\rangle = 1$. Then the constraint (7) may be rewritten in a symmetrized form which is convenient when carrying out variations:

$$\langle \Phi|P_u|\Phi\rangle = 0, \quad P_u = |\widetilde{u}\rangle\langle \widetilde{u}|. \tag{9}$$

Multiplying Eq. (9) by an arbitrary real multiplier λ and adding this to the Rayleigh quotient (4), we get the functional

$$L(\Phi) = \langle \Phi|(H + \lambda P_u)|\Phi\rangle / \langle \Phi|\Phi\rangle, \quad \Phi \in M. \tag{10}$$

We can immediately write the stationary condition for (10) as

$$\delta L(\Phi) = 0. \tag{11}$$

Using Eq. (3), the variations can be written in the form

$$|\delta \Phi\rangle = P|\delta \Phi\rangle + \sum_{a=1}^{r} (\partial_a P)|\Phi\rangle \delta \rho_a. \tag{12}$$

In this equation and in the following, we use the notation $\partial_a P \equiv \partial P / \partial \rho_a$ for simplicity.

The first term in Eq. (12) corresponds to variations within the finite-dimensional subspace M, whereas the second term allows this subspace to be rotated within Hilbert space X. Substituting Eq. (12) into the functional $L(\Phi)$, Eq. (10), and taking account of the independence and the arbitrariness of variations, we arrive at the equations

$$P(H + \lambda P_u - E)P|\Phi\rangle = 0, \tag{13}$$

and

$$\langle \Phi|(\partial_a P)(H + \lambda P_u)P|\Phi\rangle = 0. \tag{14}$$

Equation (13) is an eigenvalue problem on the subspace $M = PX$ for the modified operator

$$H_{\text{mod}} = P(H + \lambda P_u)P. \tag{15}$$

Equation (14) allows the basis set parameters to be determined by means of the variational principle and thus the optimal position of M in X can be found. However, the Lagrangian multiplier λ is as yet undetermined and condition (7) is not satisfied.

We now introduce the key theorem of the asymptotic projection method [6, 8]:

> If it is assumed that the vector $|\widetilde{u}\rangle$ is not an eigenstate of the operator PHP, then the constraint vector $|\widetilde{u}\rangle$ tends to an eigenvector of the modified operator H_{mod}, *if and only if*
>
> $$\lambda \longrightarrow \pm\infty. \tag{16}$$

This theorem ensures that the constraint condition (7) will be automatically fulfilled because of the orthogonality of the eigenvectors corresponding to different eigenvalues of a self-conjugate operator.

To prove the theorem (16), we consider the action of H_{mod} on the vector $|\widetilde{u}\rangle$. Let $|e_k\rangle$, $k = 0, 1, \ldots, n$ be the basis set vectors in the subspace M. Without loss of generality, we may assume that $|e_1\rangle = |\widetilde{u}\rangle$ and $\langle e_i|e_j\rangle = \delta_{ij}$. The matrix corresponding to H_{mod} in the chosen basis is multiplied by the vector $|\widetilde{u}\rangle$, which is represented, in the same basis set, by a column vector $[1, 0, \ldots, 0]^T$. Then the action of H_{mod} on the vector $|\widetilde{u}\rangle$ can be written in the following matrix form [6]:

$$\begin{pmatrix} H_{11} + \widetilde{\lambda} & H_{12} & \ldots & H_{1n} \\ H_{21} & H_{22} & \ldots & H_{2n} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ H_{n1} & H_{n2} & \ldots & H_{nn} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ \cdot \\ \cdot \\ 0 \end{pmatrix} = \widetilde{\lambda} \begin{pmatrix} H_{11}/\widetilde{\lambda} + 1 \\ H_{21}/\widetilde{\lambda} \\ \cdot \\ \cdot \\ H_{n1}/\widetilde{\lambda} \end{pmatrix}. \tag{17}$$

Here $H_{ik} = \langle e_i|H|e_k\rangle$, $\widetilde{\lambda} = \lambda \langle u|P|u\rangle$, and $\langle u|P|u\rangle > 0$. It is can be seen immediately that Eq. (17) becomes the eigenvalue problem for the modified operator H_{mod}, if and only if $\lambda \to \pm\infty$. Q.E.D.

As we can also see from Eq. (17), the constraint vector $|\widetilde{u}\rangle$ tends to an eigenvector of the operator H_{mod} as $1/\lambda$, therefore, $\langle u|\Phi\rangle \to 0$ as $1/\lambda$, so that the limit,

$$\lim_{\lambda \to \pm\infty} \lambda \langle u|\Phi\rangle,$$

exists. In practice, the choice of the value given to λ depends on the accuracy required. In Sects. 3 and 4, we will show that convergence behaviour is displayed for different properties. It is also clear that if $|\widetilde{u}\rangle$ is an eigenvector of PHP then it will be an eigenstate of H_{mod} for all values of λ.

The result obtained above for a single constraint vector can be easily extended to cases involving a number of constraints. In such cases, P_u in the above discussion is replaced by the orthoprojector on the subspace determined by all the constraint vectors.

We have called the technique described above the ***asymptotic projection method***.

Alternative Proof of Theorem (16)

We can require that the constraint vector $|\widetilde{u}\rangle$, which, in general, is not an eigenvector of the operator PHP, be an eigenvector of the modified operator, H_{mod}, so that

$$P(H + \lambda P_u - E_\lambda)P|\widetilde{u}\rangle = 0. \tag{18}$$

In this equation, E_λ is the, as yet unknown, eigenvalue corresponding to the vector $|\widetilde{u}\rangle$. The eigenvalue E_λ must not coincide with any eigenvalues of H_{mod}.

Let us find the value of λ for which Eq. (18) is satisfied. For this purpose Eq. (18) is rewritten, after some manipulation, in the form

$$\frac{1}{\lambda\langle u|P|u\rangle}PHP|\widetilde{u}\rangle + \left[1 - \frac{E_\lambda}{\lambda\langle u|P|u\rangle}\right]P|\widetilde{u}\rangle = 0 \tag{19}$$

where we repeat that it is assumed that the vector $|\widetilde{u}\rangle$ is not an eigenvector of the operator PHP. It is obvious that, when considered as a vector, the direction of the first term in (19) does not coincide with that of $P|\widetilde{u}\rangle$. Therefore, the fulfillment of (18) requires that each term in (1) tends to zero. This is possible if and only if $\lambda \to \pm\infty$ and $E_\lambda = \lambda\langle u|P|u\rangle$, which completes our alternative proof of theorem (16). Q.E.D.

It should be noted that, for an operator bounded from below, E_λ must be positive and $\lambda \to +\infty$. The eigenvalues are found by minimization. If we are dealing with an operator bounded from above then $\lambda \to -\infty$ and the eigenvalues are determined by maximization procedure.

2.2 Equivalence of the Original and Modified Problem

The problem defined in Eqs. (5) and (6), or in the corresponding constrained minimization problem defined in Eqs. (4) and (7), implies that the solutions are sought in the subspace $(P - P_u)X$. This is an eigenvalue problem for the effective operator $H_{\mathrm{eff}} = (P - P_u)H(P - P_u)$.

In order to clarify the validity of replacing the constrained minimization problem, Eqs. (4) and (7), by unconstrained problem, Eq. (10), we shall demonstrate that the spectra of the original operator PHP and the modified operator H_{mod} are identical

on the subspace $(P - P_u)X$ when $\lambda \to \pm\infty$. Indeed, since $|\tilde{u}\rangle$ is an eigenvector of H_{mod}, the subspace M can be written as a direct sum of subspaces [16]

$$M = (P - P_u)X \oplus P_u X \tag{20}$$

which are invariant for the operator H_{mod}. Therefore, Eq. (13) is equivalent to the eigenvalue problem on the subspace $P_u X$, for which the solution is known (the eigenvector $|\tilde{u}\rangle$ and the corresponding eigenvalue $E_\lambda \to \infty$), i.e.

$$P_u(H - E_\lambda)P_u |\Phi\rangle = 0, \ \ E_\lambda \to \infty \tag{21}$$

and equation on the subspace $(P - P_u)X$

$$(P - P_u)(H - E)(P - P_u)|\Phi\rangle = 0. \tag{22}$$

Here we used the fact that $\lambda(P - P_u)P_u(P - P_u) = 0$ for any value of λ.

Equation (22) implies that the spectra of the operators $(P - P_u)(H + \lambda P_u)(P - P_u)$ and $(P - P_u)H(P - P_u)$ are identical. However, from practical point of view, Eq. (13) is much simpler to solve than Eq. (22). Indeed, Eq. (22) requires additional calculations of $\langle\Phi|H|u\rangle$ and $\langle u|H|u\rangle$, whereas Eq. (13) requires only the overlap element $\langle\Phi|u\rangle$. (Further discussion of these practicalities is given in Sect. 2.3).

2.3 Comparison with Other Methods

There are several techniques for solving the problem defined in Eqs. (1) and (2) or their variational implementation, Eqs. (5) and (6). (See e.g. the texts by Himmelblau [4] and by Gill and Murray [5], and the papers by Feshbach [17], by Weeks and Rice [18] and by Huzinaga [19], and references therein). A natural solution of this problem is to derive the equations for the constrained function in such a manner that the orthogonality constraints are built into the variational procedure as an auxiliary condition. Traditionally, this can either be achieved by the method of Lagrangian multipliers or the projection operator technique. In the discussion below, we shall demonstrate the main features which distinguish our asymptotic projection method from other existing methods. The traditional methods of the elimination of Lagrangian multipliers and the projection operators will be described in more detail since many other approaches can be reduced to these techniques.

2.3.1 Elimination of Off-Diagonal Lagrangian Multipliers Method

We shall follow closely here the presentation given in Chapter 2 of Hurley's well-known book *Introduction to the electron theory of small molecules* [20].

The electronic Schrödinger equation for some molecular system may be written

$$H\Psi_i = E_i\Psi_i \tag{23}$$

where H is the electronic Hamiltonian and the eigenfunctions $\Psi_0, \Psi_1, \ldots$ may be chosen as a complete, orthonormal set, ordered in terms of the energy eigenvalues $E_0, E_1, \ldots$, so that

$$E_i \leqslant E_{i+1} \tag{24}$$

and

$$\langle \Psi_i | \Psi_j \rangle = \delta_{ij}. \tag{25}$$

Now the electronic Schrödinger Eq. (23) may be regarded as the condition that the energy expectation value

$$E = \langle \Psi | H | \Psi \rangle \tag{26}$$

should remain stationary for arbitrary variations $\delta \Psi$ of the many-electron wave function Ψ, which maintain the normalization condition

$$\langle \Psi | \Psi \rangle = 1. \tag{27}$$

In studies of excited states and in self-consistent field theory it is sometimes necessary to impose additional linear constraints on the wave function and the admissible variations. A linear constraint may be expressed as the orthogonality of Ψ to some fixed constraint function $u(\mathbf{r})$

$$\langle \Psi | u \rangle = \langle u | \Psi \rangle = 0, \tag{28}$$

which is taken to be normalized

$$\langle u | u \rangle = 1. \tag{29}$$

The constraints (27) and (28) can be incorporated by means of Lagrange multipliers E, ε and η, by considering the functional

$$L = \langle \Psi | H | \Psi \rangle - E \langle \Psi | \Psi \rangle - \varepsilon \langle \Psi | u \rangle - \eta \langle u | \Psi \rangle \tag{30}$$

and requiring that

$$\delta L = 0 \tag{31}$$

for arbitrary variations $\delta \Psi$ and suitably chosen values of E, ε and η. Exploiting the hermiticity of H, the condition (31) can be written in the form

$$\langle \delta \Psi | (H - E) | \Psi \rangle - \varepsilon \langle \delta \Psi | u \rangle + \langle \Psi | (H - E) | \delta \Psi \rangle - \eta \langle u | \delta \Psi \rangle = 0. \tag{32}$$

Since the variations $\langle \delta \Psi |$ and $| \delta \Psi \rangle$ are arbitrary, the condition (32) leads to two equations which can be written

$$H | \Psi \rangle = E | \Psi \rangle + \varepsilon | u \rangle \tag{33}$$

and

$$\langle \Psi | H = E \langle \Psi | + \eta \langle u |. \tag{34}$$

Comparing Eq. (33) with the complex conjugate of (34) leads to the conclusion that the off-diagonal Lagrange multipliers are related by

$$\eta = \varepsilon^*. \tag{35}$$

Imposing the condition (35) renders Eq. (34) equivalent to Eq. (33) so that the former may be dropped.

The values of the constants E and ε are found by multiplying Eq. (33) by $\langle\Psi|$ or by $\langle u|$, i.e.

$$E = \langle\Psi|H|\Psi\rangle \tag{36}$$

and

$$\varepsilon = \langle u|H|\Psi\rangle \tag{37}$$

Equation (33), together with the orthonormality conditions (27) and (28), provides the solution to our variational problem. Because of the second term on the right hand side the form of Eq. (33) is not that of an equation determining the eigenvalues and eigenfunctions of some Hermitian operator. However, it may be reduced to this standard form by introducing a suitable effective Hamiltonian. Indeed, taking the expression (37) into account, Eq. (33) can be rewritten in a form

$$H|\Psi\rangle - |u\rangle\langle u|H|\Psi\rangle = E|\Psi\rangle. \tag{38}$$

Using the definition of the orthoprojector

$$P_u = |u\rangle\langle u|, \tag{39}$$

$$P_u^2 = P_u \tag{40}$$

the Eq. (38) takes a form

$$H|\Psi\rangle - P_u H|\Psi\rangle = E|\Psi\rangle. \tag{41}$$

Generally speaking the operator $P_u H$ is not Hermitian, however the symmetrized product $P_u H + H P_u$ is necessarily Hermitian. Since $H P_u|\Psi\rangle = 0$ we arrive at the eigenvalue equation for the effective operator

$$H_{\text{eff}}^{[1]}|\Psi\rangle = E|\Psi\rangle \tag{42}$$

with

$$H_{\text{eff}}^{[1]} = H - (P_u H + H P_u). \tag{43}$$

It is easy to show that the vector $|u\rangle$ itself is an eigenvector of $H_{\text{eff}}^{[1]}$ with the eigenvalue $E_u = -\langle u|H|u\rangle$ and then the constraint (28) is automatically fulfilled due to orthogonality of eigenfunctions of $H_{\text{eff}}^{[1]}$.

2.3.2 Projection Operator Techniques and Other Methods

Following the work of Huzinaga and Cantu [21] and the more recent work of Surjan [3], we now consider the variational procedures based on the projected function

$$|\Psi\rangle = (I - P_u)|\Phi\rangle \tag{44}$$

which satisfies the constraint $\langle\Psi|u\rangle = 0$ for any $|\Phi\rangle$. Variation of the Rayleigh quotient

$$\delta E(\Psi) = \delta[\langle\Psi|H|\Psi\rangle/\langle\Psi|\Psi\rangle,] \tag{45}$$

leads to the Euler equation

$$[(I - P_u)H(I - P_u) - E(I - P_u)|\Phi\rangle = 0 \tag{46}$$

which can be interpreted as an eigenvalue problem for an effective Hermitian operator $H_{\text{eff}}^{[2]}$

$$H_{\text{eff}}^{[2]}|\Phi\rangle = E(I - P_u)]|\Phi\rangle \tag{47}$$

where

$$H_{\text{eff}}^{[2]} = H + E_u P_u - P_u H - H P_u \tag{48}$$

and $E_u = \langle u|H|u\rangle$.

It easy to verify that the projected excited functions $\Psi_i = (I - P_u)\Phi_i$ corresponding to different solutions of Eq. (47) will be orthogonal to each other. We may also observe that there is a close relation between the effective operator defined in Eq. (43) for the elimination of off-diagonal Lagrangian multipliers method and $H_{\text{eff}}^{[2]}$ defined in Eq. (21) for the projection operator technique.

Both the elimination of off-diagonal Lagrangian multipliers method and the projection operator technique require the evaluation of matrix elements of the form $\langle u|H|\Phi\rangle$ whereas the asymptotic projection method only involves overlap elements $\langle u|\Phi\rangle$, which are more easily computed. This difference in computational demands can be particularly significant when minimization is carried out with respect to non-linear basis set parameters (i.e. exponents). For example, in self-consistent field calculations for excited state the elimination of off-diagonal Lagrangian multipliers method and the projection operator technique require the evaluation of $\sim m^4$ elements of the Fock operator whereas only $\sim m^2$ overlap elements are required for the asymptotic projection method, where m is dimension of one-particle basis set employed.

We comment briefly on a method for handling the orthogonality constraints in the self-consistent field theory developed by Colle, Fortunelli and Salvetti [22, 23]. The solution to the constrained variational problem presented by these authors is specific to the Hartree-Fock case. In contrast, the asymptotic projection method described in the present work is based on the properties of self-conjugate operators. It is a general method which can be applied to many systems and in many approximation schemes. In our accompanying paper [24], we shall demonstrate the

application of the asymptotic projection method to self-consistent field problems with orthogonality constraints.

The asymptotic projection method described in Sect. 2.1 may seem similar to the shift operator technique introduced by Huzinaga [19]. This technique was found to be useful for shifting the positions of eigenvalues in the spectrum of the Fock operator in the Hartree-Fock theory thereby accelerating the convergence of the iterative self-consistent field process. However, it is known [19] that this technique operates only on the exact eigenvectors of the operator PHP, whereas in the asymptotic projection method *arbitrary* constraint vectors are considered.

We also note the similarity of the asymptotic projection method to techniques for incorporating orthogonality constraints by means of an energy penalty term. However, we recognize that this penalty term method requires several calculations of a functional (e.g. the energy functional) in order to determine an optimal value of the multiplier λ. There have been some preliminary attempts to apply the penalty term method to excited state calculations. The reader is referred to the work of Dutta and Bhattacharya [25], where different penalty functions are considered.

In concluding this section, we note that, from practical point of view, the numerical solution of the eigenvalue equation for the operator H_{mod} is a stable process, although the condition number (i.e. ratio $E_{\text{max}}/E_{\text{min}}$) of the corresponding matrix can be quite large. The problem is that the sensitivity of the eigenvalue is measured by the condition number of diagonalizing matrix rather than the H_{mod} matrix [26].

3 Application to Excited State Problems

It is well known that the *ab initio* study of the excited electronic states of atoms and molecules contains elements which are not present in the treatment of ground states. In particular, excited state wave functions must be orthogonal to states of lower energy. For the lowest eigenstate in a given symmetry class, a trial wave function of that symmetry is automatically orthogonal to all lower eigenstates. For higher eigenstates, the imposition of the orthogonality constraints is often difficult and cumbersome.

The asymptotic projection method described above can be directly applied to the calculation of approximate wave functions and energies of excited states having the same spin and spatial symmetry as lower states. In this case, $u = \Phi_0$ and E_0 are an approximate ground state wave function and the corresponding ground state energy respectively. E_0 is defined as the lowest root of Eq. (13) at $\lambda = 0$. The operator H is the Hamiltonian of a system. The first excited state or the second eigenvalue is then defined by the relation

$$E_1 = E(\Phi_1) = \langle \Phi_1 | H | \Phi_1 \rangle = \min_{\Phi \in (\Phi_0)^{\perp}} E(\Phi), \quad \langle \Phi_1 | \Phi_1 \rangle = 1 \qquad (49)$$

where the minimum is taken with respect to all vectors $|\Phi\rangle$ belonging to the orthogonal complement $(\Phi_0)^{\perp}$ of the vector $|\Phi_0\rangle$, i.e. the vectors $|\Phi\rangle \in (\Phi_0)^{\perp}$ satisfy the

condition $\langle \Phi | \Phi_0 \rangle = 0$. It should be stressed that, in general, $(\Phi_0)^\perp \not\subseteq M$, i.e., a subspace distinct from M can be used for E_1. Higher eigenvalues are determined in a similar fashion.

3.1 Bounds to Excited State Energies

Löwdin [27] has published a clear and detailed discussion of the general problem of variation in a restricted subspace. He has documented some of the technical difficulties that arise in using Eq. (49). In particular, we must require orthogonality of an excited state eigenfunction to the exact lower eigenfunctions of H if the minimum given by Eq. (49) is to be an upper bound to the exact eigenstate energy. A more practical formulation, which avoids the need for the exact lower eigenfunctions, has been given by Hylleraas and Undheim [28] and by MacDonald [29]. These authors have shown that convenient upper bounds are provided by the Rayleigh-Ritz method if the functions $|\Phi_i\rangle$ are determined in the *same* basis set $|\phi_k\rangle (k = 0, 1, \ldots, n)$ using the expansion given in Eq. (3).

If we use different basis sets for different states, then the imposition of the orthogonality constraint (7) with respect to an approximate wave function for a lower state does not, in general, yield an excited state energy which is an upper bound to the exact excited state energy. However such an approximation is often preferable since it can provide a more compact and accurate representation of the eigenvectors and eigenvalues. *"The desirability of using different basis sets for different states"* was pointed out by Shull and Löwdin [30] as long ago as 1958. Of course such a scheme requires significant computation, but, given the availability of an efficient method for solving the eigenvalue problem (1) with orthogonality constraints (2), it can be justified. In this case, the quality of the bounds to the excited state energies remains an open question.

Although the imposition of the orthogonality constraint (7) to an approximate lower state wave function does not, in general provide an upper bound to the excited state, there exists a so-called "weak bound" (introduced by Zener and coworkers [31]) with respect to the exact energies $\mathscr{E}_i$:

$$E_i \geq \mathscr{E}_i - \sum_{j}^{i-1} \delta_j (\mathscr{E}_i - \mathscr{E}_j). \tag{50}$$

In this equation,

$$\delta_j = 1 - |\langle \Phi_i | \Psi_j \rangle|^2 \tag{51}$$

and Ψ_j is the exact wave function for the j-th state. We can obtain an upper bound by imposing the additional constraint

$$\langle \Phi_i | H | \Phi_j \rangle = 0. \tag{52}$$

It should be noted that the asymptotic projection method can also be applied to the problem defined by Eq. (52).

In practical calculations, the excited state energies are expected to lie above the the exact energies if Φ_0 is a good approximation to the true ground state eigenfunction. Therefore, we shall now investigate the bounding properties when only the orthogonality constraint (7) is imposed on an excited function. In this case, it is our opinion that a $\min - \max$ principle [16], which is not directly based on eigenvectors is useful. For example, for the first excited state we have

$$E_1 = \max_{\Phi_0} \min_{\Phi \in (\Phi_0)^\perp} E(\Phi). \tag{53}$$

In this equation, the maximum is attained when Φ_0 is equal to the exact wave function Ψ_0 of the ground state.

Equation (53) suggest that the value of E_1 is influenced by two effects. On the one hand, if a complete basis set is used for Φ_0 then a finite-dimensional approximation to the excited state leads to an upper bound for E_1, i.e. $E_1 \geq \mathscr{E}_1$. On the other hand, if the variation of Φ is carried out in the subspace $(I - |\Phi_0\rangle\langle\Phi_0|)X$ and a finite basis set approximation is made for Φ_0, then the $\min - \max$ principle (53) gives $\mathscr{E}_1 \geq E_1$, that is E_1 is a lower bound to the true energy with the equality applying in the case $\Phi_0 = \Psi_0$.

The imposition of the orthogonality constraint $\langle\Phi_1|\Phi_0\rangle = 0$ alone does not guarantee that E_1 will be an upper bound to the exact energy. However, in contrast to the "weak bound" defined in Eq. (50), we are able to give a relation between E_1 and an upper bound E_1^{upper} [12, 13, 32] which proves useful from the point of view of practical calculations. Indeed, for the approximate wave functions Φ_0 and Φ_1, the secular determinant may be written

$$\det \begin{vmatrix} \langle\Phi_0|H|\Phi_0\rangle - \varepsilon & \langle\Phi_0|H|\Phi_1\rangle \\ \langle\Phi_1|H|\Phi_0\rangle & \langle\Phi_1|H|\Phi_1\rangle - \varepsilon \end{vmatrix} = 0. \tag{54}$$

This equation has two solutions which may be written

$$E_0^{\text{upper}} = \frac{1}{2}[E_0 + E_1] - \frac{1}{2}\left[(E_0 - E_1)^2 + 4|H_{01}|^2\right]^{\frac{1}{2}} \tag{55}$$

$$E_1^{\text{upper}} = \frac{1}{2}[E_0 + E_1] + \frac{1}{2}\left[(E_0 - E_1)^2 + 4|H_{01}|^2\right]^{\frac{1}{2}} \tag{56}$$

where the off-diagonal matrix element is $H_{01} = \langle\Phi_0|H|\Phi_1\rangle$. Using the Hylleras-Undheim-MacDonald theorem [29], we know that the solutions of the secular equations are upper bounds and, in particular,

$$E_1^{\text{upper}} \geqslant \mathscr{E}_1. \tag{57}$$

Furthermore, we note that

$$\left|E_0^{\text{upper}} - E_0\right| = \left|E_1^{\text{upper}} - E_1\right| \tag{58}$$

and so, if the ground state energy is determined to given accuracy then E_1 will have a comparable accuracy and the coupling matrix elements, H_{01}, may be neglected at this level of approximation.

3.2 Gradient of the Excited State Energy with Respect to Basis Set Parameters

There is, at present, no published analytical expression for the gradient of the energy of an excited state with respect to basis set parameters for excited states having the same symmetry as the ground state. The formalism developed in Sect. 2.1 allows us to derive a suitable expression. Indeed, the left-hand side of Eq. (14) represents the components of the gradient of the energy of the excited state $\partial_a E_1$ with respect to nonlinear basis set parameters ρ_a, i.e.

$$\partial_a E_1 = 2\langle \Phi_1 | (\partial_a P)(H + \lambda P_u) P | \Phi_1 \rangle, \tag{59}$$

In this equation, $P_u = |\Phi_0\rangle\langle\Phi_0|$. The factor of 2 arises from the complex conjugate which is equal to the real part.

Practical application of Eq. (59) requires knowledge of the limit

$$\lim_{\lambda \to \infty} \lambda \langle \Phi_0 | \Phi_1 \rangle. \tag{60}$$

This limit can be found from Eq. (13) which can be rewritten as

$$P(H - E_1)P|\Phi_1\rangle = -\lambda|\Phi_0\rangle\langle\Phi_0|\Phi_1\rangle. \tag{61}$$

Multiplying the left-hand side of Eq. (61) by $\langle\Phi_0|$, we obtain a relation which is valid for any value of λ:

$$\lambda\langle\Phi_0|\Phi_1\rangle = -\langle\Phi_0|P(H - E_1)P|\Phi_1\rangle, \tag{62}$$

or

$$\lim_{\lambda \to \infty} \lambda\langle\Phi_0|\Phi_1\rangle = -\langle\Phi_0|PHP|\Phi_1\rangle. \tag{63}$$

Substituting Eq. (63) in Eq. (59), we arrive at the following expression

$$\partial_a E_1 = 2\langle\Phi_1|(\partial_a P)H|\Phi_1\rangle - 2\langle\Phi_1|(\partial_a P)|\Phi_0\rangle\langle\Phi_0|PHP|\Phi_1\rangle, \tag{64}$$

which is the gradient of the excited state energy with respect to non-linear basis set parameters.

It should be emphasised that when a common basis set is used in the description of both the ground state and the excited state with the corresponding projection operator P, then

$$\lim_{\lambda \to \infty} \lambda \langle \Phi_0 | \Phi_1 \rangle = 0, \tag{65}$$

because $PHP|\Phi_0\rangle = E_0|\Phi_0\rangle$ and

$$\lim_{\lambda \to \infty} \langle \Phi_0 | \Phi_1 \rangle = 0. \tag{66}$$

Furthermore, we can write

$$\langle \Phi_1 | (\partial_a P) | \Phi_0 \rangle = \langle \Phi_1 | P (\partial_a P) P | \Phi_0 \rangle = 0, \tag{67}$$

since $P(\partial_a P)P = 0$ because of the properties of the orthoprojectors. Thus, expression (59) for the gradient of the excited state energy with respect to nonlinear basis set parameters can be simplified and written as

$$\partial_a E_1 = 2 \langle \Phi_1 | (\partial_a P) H | \Phi_1 \rangle. \tag{68}$$

This formulae is similar to that for the gradient of the ground state energy (see e.g. the paper by two of us [33])

For the purposes of practical calculations, the operators contained in Eqs. (64) and (68) can be expressed in terms of basis set functions ϕ_i if the derivatives of the projection operator are taken into account

$$\partial_a P = \sum_{k=0}^{n} \left[(I - P) | \partial_a \phi_k \rangle \langle \phi_k | + | \phi_k \rangle \langle \partial_a \phi_k | (I - P) \right]. \tag{69}$$

In this equation

$$|\phi_k\rangle = \sum_{j=0}^{n} |\phi_j\rangle S_{jk}^{-1} \tag{70}$$

where S_{jk}^{-1} is an element of the inverse of the overlap matrix.

4 Illustrative Excited State Calculations of One-Electron Molecular Systems H_2^+ and H_3^{++}

The diatomic and triatomic molecular ions H_2^+ and H_3^{++} are the simplest molecular systems for which the exact numerical solutions of the Schrödinger's equation are known. For these systems numerical solutions are available to "machine accuracy" [34,35]. These numerical solutions provide excellent "benchmarks" for testing more approximate methods which have been developed for solving more complex problems.

For the H_2^+ ion, we studied both the ground state $1\sigma_g$ ($1s\,\sigma_g$) and the first excited state of the same symmetry $2\sigma_g$ ($2s\,\sigma_g$). The nuclear separation was set at 2.0 bohr.

For this geometry, the exact ground state electronic energy is $-0.602\,634\,214\,494\,9$ Hartree whereas the exact electronic energy of the $2\sigma_g$ $(2s\,\sigma_g)$ excited state is $+0.139\,135\,124\,661\,7$ Hartree [34]. The difference between these two exact energies is $+0.741\,769\,339\,156\,6$ Hartree.

In the present study, we employed basis sets of s-type Gaussian functions centred on the internuclear axis with both exponents and positions determined by invoking the variational principle. Specifically, we used basis sets containing $2n+1$ functions distributed along the internuclear axis with $n = 3, 4, ..., 13$. For an odd number of basis function, symmetry considerations require that a single function is placed at the bond mid-point and the remaining functions are arranged in pairs symmetrically about this mid-point. We compared the energies supported by finite basis set expansions with the corresponding exact values. In particular, we carried out calculations using two schemes in the construction of basis sets: in the first, we used a common basis set for the different states, whilst in the second, different basis sets were employed for different states. We used basis sets consisting of $2 \times 13 + 1$ functions to compare the two approaches. In order to assess the effects of basis set truncation on the calculated energies and energy differences, we also used smaller basis sets, designated $2 \times 5 + 1$ and $2 \times 8 + 1$.

4.1 Common Basis Set for Different States

The parameters defining an optimized distributed basis set consisting of $(2 \times 13 + 1)$ s-type Gaussian functions for the ground state of the H_2^+ ion with a nuclear separation of 2.0 bohr can be found in Ref. [13]. The energies supported by this basis set for the $1\sigma_g$ $(1s\,\sigma_g)$ and $2\sigma_g$ $(2s\,\sigma_g)$ states of the hydrogen molecular ion are collected in Table 1. In this table, the column headed Δ displays the difference between

Table 1 Total energies (in Hartrees) for the H_2^+ molecular ion, with the nuclear separation of 2.0 bohr, calculated using the constrained variational method and a common basis set for different states

State	Basis set	E	Δ^{a}
$2\sigma_g$ $(2s\,\sigma_g)$	$(2 \times 13 + 1)$	$+0.151\,939\,303$	12804.178
	$(2 \times 8 + 1)$	$+0.157\,581\,881$	18446.756
$[+0.139\,135\,124\,661\,7]$	$(2 \times 5 + 1)$	$+0.199\,485\,926$	60350.801
$1\sigma_g$ $(1s\,\sigma_g)$	$(2 \times 13 + 1)$	$-0.602\,633\,875$	0.339
	$(2 \times 8 + 1)$	$-0.602\,623\,992$	10.222
$[-0.602\,634\,214\,494\,9]$	$(2 \times 5 + 1)$	$-0.602\,512\,544$	121.670
$\Delta E_{1\sigma_g\,(1s\,\sigma_g),2\sigma_g\,(2s\,\sigma_g)}$	$(2 \times 13 + 1)$	$+0.754\,573\,178$	12803.839
	$(2 \times 8 + 1)$	$+0.760\,205\,873$	18436.534
$[+0.741\,769\,339\,156\,6]$	$(2 \times 5 + 1)$	$+0.801\,998\,470$	60229.131

$^{\text{a}}$ $- \Delta$ (in μ Hartrees) is the difference between the energy expectation value supported by the asymptotic projection method and the corresponding exact value.

the energy expectation value supported by the asymptotic projection method and the corresponding exact value.

For the constrained variational method with a common basis set for different states, the calculated ground and the excited state total energies become increasingly accurate with increasing size of basis set. Consequently, the accuracy of the calculated energy difference, ΔE also increases with the size of the basis set. However, the error in the calculated energy for the excited state is very much larger than that for the ground state. The error in the excited state energy is almost 500 times that in the ground state energy for the the $(2 \times 5 + 1)$ basis set and roughly 4×10^4 times the corresponding energy for the $(2 \times 13 + 1)$ basis set. This is not surprising since the basis sets are optimized for the ground state and therefore describe the ground state with increasing accuracy relative to the excited state as the basis set is extended. The error in the calculated total energy for the excited state dominates the error in the energy difference, ΔE.

4.2 Different Basis Sets for Different States

The parameters for the distributed basis set consisting of $(2 \times 13 + 1)$ s-type Gaussian functions optimized for the excited state of the H_2^+ ion, with a nuclear separation of 2.0 bohr, can be found in Ref. [13]. Again, for basis sets containing an odd number of functions, there is one function centred on the bond mid-point with the remaining functions arranged symmetrically The pairs of exponents and z-coordinates are taken to be ordered according to their distance from the bond mid-point.

For calculations using the constrained variational method with different basis sets for different states, the orthogonality of the ground and excited state wavefunctions was imposed by solving the eigenproblem defined in Eq. (13) with

$$\lambda = 5 \times 10^4 \text{a.u.} \tag{71}$$

This value of λ was determined so as to ensure that

$$\langle \Phi_0 | \, \Phi_1 \rangle = 0.000000000. \tag{72}$$

As we have already mentioned, the accuracy with which the orthogonality constraint is satistifed as a function of λ depends on specific features of the particular problem under consideration.

In the case of the hydrogen molecular ion, we show in Fig. 1 that the value λ ~ 5–10 hartree ensures the overlap integral value $\langle \Phi_0 | \Phi_1 \rangle < 10^{-7} - 10^{-8}$. As can be seen, the ground state-to-excited state transition occurs almost step-wise within the narrow range of $\lambda \sim 0.74 - 0.75$ hartree that corresponds to the excitation energy value (see ΔE from Table 1). In addition we observed that for a wide range $0.75 < \lambda < 10^4$, the value E_1 remains almost constant, indicating the stability of the solution achieved by the method.
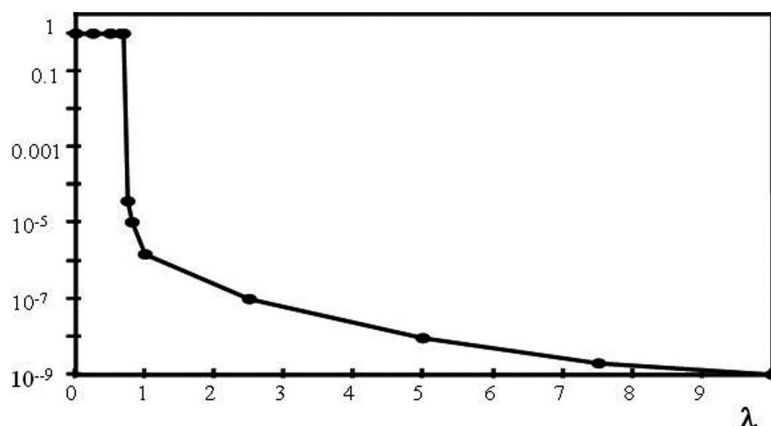
Fig. 1 The value of the overlap integral $\langle \Phi_0 | \Phi_1 \rangle$ as a function of the parameter λ for the ground state of the H_2^+ molecular ion with $R = 2.0$ bohr. Φ_0 and Φ_1 were calculated using a basis set optimized for the first excited state

Table 2 Total energies (in Hartrees) for the H_2^+ molecular ion, with the nuclear separation of 2.0 bohr, calculated using the constrained variational method and different basis sets for different states

State	Basis set	E	Δ^a
$2\sigma_g\ (2s\,\sigma_g)$	$(2 \times 13 + 1)$	$+0.139\,135\,657$	0.532
	$(2 \times 8 + 1)$	$+0.139\,148\,302$	13.177
$[+0.139\,135\,124\,661\,7]$	$(2 \times 5 + 1)$	$+0.139\,216\,795$	81.670
$1\sigma_g\ (1s\,\sigma_g)$	$(2 \times 13 + 1)$	$-0.602\,633\,875$	0.339
	$(2 \times 8 + 1)$	$-0.602\,623\,992$	10.222
$[-0.602\,634\,214\,494\,9]$	$(2 \times 5 + 1)$	$-0.602\,512\,544$	121.670
$\Delta E_{1\sigma_g\,(1s\,\sigma_g),2\sigma_g\,(2s\,\sigma_g)}$	$(2 \times 13 + 1)$	$+0.741\,769\,532$	0.193
	$(2 \times 8 + 1)$	$+0.741\,772\,294$	2.955
$[+0.741\,769\,339\,156\,6]$	$(2 \times 5 + 1)$	$+0.741\,729\,339$	-40.000

[a] – Δ (in μ Hartrees) is the difference between the value of the energy (or excitation energy) obtained with the asymptotic projection method and the corresponding exact value.

The energies supported by the $(2 \times 5 + 1)$, $(2 \times 6 + 1)$ and $(2 \times 13 + 1)$ basis sets for the $1\sigma_g\ (1s\,\sigma_g)$ and $2\sigma_g\ (2s\,\sigma_g)$ states of the hydrogen molecular ion are collected in Table 2.

The accuracy of the excited state energies obtained by employing different basis sets for different states in the constrained variational method are much improved over those given in Table 1 for the common basis set case. For the $(2 \times 5 + 1)$ basis set, the error in the calculated excited state energy displayed in Table 2 is 739 times smaller than the corresponding error in Table 1. This error is reduced by a factor of 24,000 for the $(2 \times 13 + 1)$ basis set. This reduction in the error is not surprising because the basis sets are optimized for the respective states. The

Table 3 Electronic energies for the ground state, the first excited state and excitation energy (all in Hartrees) of linear H_3^{2+} for $R_{AB} = R_{BC} = 2$ bohr

Method	$E(GS)$	$E(ES)$	$E(ES) - E(GS)$
Present work	$-1.524\ 159\ 62$	$-1.173\ 373\ 83$	$0.350\ 785\ 79$
Exact	$-1.524\ 159\ 90$	$-1.173\ 374\ 30$	$0.350\ 785\ 60$
Δ^{a}	0.28	0.47	0.19

$^{\text{a}}$ $-\Delta$ is the difference between the value of the energy obtained with the asymptotic projection method and the corresponding exact value.

constrained variational approach with different basis sets for different states yields the most accurate energies for a basis set of a given size. However, this approach also leads to the greatest computational demands. (Although these demands are small for the systems considered in the present work.) The calculated energy differences, ΔE, displayed in Table 2 using different basis sets for different states are also markedly improved over those given in Table 1. It should be noted that ΔE, is not an upper bound to its exact value as the results presented in Table 2 clearly demonstrate. The total energies and the energy differences converge with increasing size of basis set. In fact, the magnitude of ΔE decreases monotonically with the size of the basis set. For the excited state, the convergence pattern with increasing size of basis set size mirrors that observed for the ground state.

For our study of the linear H_3^{2+} molecular ion, the nuclei were positioned at $(0.0, 0.0, -2.0)$, $(0.0, 0.0, 0.0)$ and $(0.0, 0.0, +2.0)$ bohr. For this configuration, Hackel et al [35] reported a ground (1σ) state electronic energy of $-1.524\ 159\ 9$ hartree whilst for the first excited (2σ) state they determined an electronic energy of $-1.173\ 374\ 3$. These authors used the finite element method to perform their calculations. The present calculations were carried out by using an optimized basis set of s-type Gaussian functions constructed in a similar fashion to the sets employed for the H_2^+ ion. In Table 3, calculated electronic energies of the linear H_3^{2+} ion are displayed for the ground state and the excited state as well as the corresponding excitation energy. The energies presented in Table 3 were supported by the largest basis set employed in this study containing a total of 42s functions. This basis set is defined in Table 4.

The results presented above for the diatomic H_2^+ ion and the triatomic H_3^{++} ion demonstrate that the asymptotic projection method is capable of supporting an accuracy of $\sim 1\ \mu$Hartree for excited state energies for one-electron systems when used in conjunction with optimized basis sets. Of course, the method described here can be applied to many-electron molecular systems where they can support a comparable accuracy.

Table 4 Optimal basis set parameters for the ground state (1σ) and excited state (2σ) of the linear H_3^{++} ion. The exponents, ζ_p, and positions, z_p, are variationally optimized for each state. The nuclei are located at the points $(0,0,-2)$, $(0,0,0)$ and $(0,0,2)$[a]

	1σ			2σ	
p	ζ_p	z_p	p	ζ_p	z_p
1,2	0.8418205(0)	±0.1910288(1)	1,2	0.7639302(0)	±0.1875791(1)
3,4	0.3476880(0)	±0.1650485(1)	3,4	0.3019611(0)	±0.1485761(1)
5,6	0.1517923(1)	±0.9561177(0)	5,6	0.1742844(1)	±0.4554557(0)
7,8	0.1339805(1)	±0.1838749(1)	7,8	0.8208070(0)	±0.1851638(1)
9,10	0.2381616(1)	±0.1917609(1)	9,10	0.1692262(1)	±0.1921101(1)
11,12	0.6478234(1)	±0.1975352(1)	11,12	0.4262420(1)	±0.1986405(1)
13,14	0.1627814(0)	±0.1641909(1)	13,14	0.1448846(0)	±0.1601241(1)
15,16	0.1929540(2)	±0.1995239(1)	15,16	0.1124180(2)	±0.1997629(1)
17,18	0.6749235(2)	±0.1997803(1)	17,18	0.3316262(2)	±0.1998046(1)
19,20	0.2959242(3)	±0.1999778(1)	19,20	0.4419684(3)	±0.1999778(1)
21,22	0.1973472(4)	±0.1999911(1)	21,22	0.2570299(4)	±0.1999911(1)
23,24	0.3684891(1)	±0.2103583(0)	23,24	0.1127609(3)	±0.1999975(1)
25,26	0.6332710(0)	±0.8738938(0)	25,26	0.5016808(1)	±0.5242137(−1)
27,28	0.2998761(1)	±0.2201661(1)	27,28	0.6567027(0)	±0.5547677(0)
29,30	0.7222268(0)	±0.3345823(1)	29,30	0.1944792(1)	±0.2210755(1)
31	0.4762336(4)	0	31,32	0.3748303(0)	±0.2355470(1)
32	0.7112966(3)	0	33,34	0.6357909(−1)	±0.1841511(1)
33	0.1618855(3)	0	35,36	0.2175831(2)	±0.1702267(−1)
34	0.4608506(2)	0	37,38	0.6985340(2)	±0.9988073(−2)
35	0.1508453(2)	0	39,40	0.4119900(1)	±0.1507338(0)
36	0.5479534(1)	0	41,42	0.2013408(5)	±0.2000000(1)
37	0.2022999(1)	0			
38	0.8570714(0)	0			
39	0.3584578(0)	0			
40	0.1779767(0)	0			
41	0.7531864(−1)	0			
42	0.3137232(−1)	0			

[a] Powers of ten are given in parentheses.

5 Concluding Remarks

We have described an alternative technique for solving a wide class of problems in quantum chemistry and in atomic and molecular physics, which can be reduced to an eigenvalue equation with some orthogonality constraints imposed on eigenvectors. This technique is based on an asymptotic projection method proposed, which was earlier and which can be simply implemented. The basic features of the asymptotic projection method have been presented and the method has been compared with conventional approaches to the constrained variational problem, namely, the elimination of off-diagonal Lagrangian multipliers method and the projection operators technique.

Some specific features of excited state calculations that implement the asymptotic projection method have been discussed. Unlike the major traditional methods where an improvement in accuracy is achieved by using extensive ways, for

instance, considerable extension of both atom-centered one-particle basis sets and increasing a number of many-particle configurations (sometimes up to several billions [36, 37]), we focused on the development alternative approaches capable of optimizing relatively small distributed basis sets.

Finally, it should be noted that the asymptotic projection method can also provide a suitable reference with respect to which a well-founded many-body expansion for correlation effects in open-shell states can be developed.

References

1. A.J. Sadlej, *Intern. J. Quantum. Chem.* **63**, 35 (1997).
2. X. Assfeld and J.-L. Rivail, *Chem. Phys. Lett.* **263**, 100 (1996).
3. P.R. Surjan, *Chem. Phys. Lett.* **325**, 120 (2000).
4. D.M. Himmelblau, *Applied Nonlinear Programming* McGraw-Hill, New York (1972).
5. P.E. Gill and W. Murray, *Numerical Methods of Constrained Optimization*, Academic Press, London, New York, San Francisco (1974).
6. V.N. Glushkov and A.Ya. Tsaune, *Zh. Vychisl. Mat. Mat. Fiz.* **25**, 298 (1985); *USSR Comp. Mathemat. Math. Phys.*, **25**, 196 (1986).
7. V.N. Glushkov, *J. Math. Chem.* **31**, 91 (2002).
8. V.N. Glushkov, *Opt. Spectrosc.* **93**, 11 (2002).
9. A.Ya. Tsaune, V.N. Glushkov and A.I. Aprashukhin, *J. Mol. Struct. (THEOCHEM)* **312**, 289 (1994).
10. V.N. Glushkov and A.Ya. Tsaune, *Chem. Phys. Lett.* **262**, 59 (1996).
11. V.N. Glushkov, *Chem. Phys. Lett.* **273**, 122 (1997).
12. V.N. Glushkov, *Chem. Phys. Lett.* **287**, 189 (1998).
13. N.I. Gidopoulos, V.N. Glushkov and S. Wilson, *Proc.R. Soc. Lond. A.* **457**, 1657 (2001).
14. V.N. Glushkov and S. Wilson, In: *Recent Advances in the Theory of Chemical and Physical Systems*, edited by J.-P. Julien et al., p.107, Springer, Dordrecht (2006).
15. V.N. Glushkov and A.Ya. Tsaune, *Opt. Spectrosc.* **87**, 267 (1999).
16. T. Kato, *Perturbation theory for linear operators*, Springer-Verlag, Berlin (1963).
17. H. Feshbach, *Ann. Phys. N.Y.* **19**, 287 (1962).
18. J.D. Weeks and S.A. Rice, *J. Chem. Phys.* **49**, 2741 (1968).
19. S. Huzinaga, *Method of molecular orbitals*, Tokyo, (1980), *Metod molekulyarnikh orbitaley* (in Russian), Mir, Moskva (1983) 461 p.
20. A.C. Hurley, *Introduction to the electron theory of small molecules*, p. 35, Academic Press, London, (1976).
21. S. Huzinaga and A.A. Cantu, *J. Chem. Phys.* **55**, 5543 (1971).
22. R. Colle, A. Fortunelli and O. Salvetti, *Theor. Chim. Acta* **71,** 467 (1987).
23. R. Colle, A. Fortunelli and O. Salvetti, *Theor. Chim. Acta* **75,** 323 (1989).
24. V.N. Glushkov, N.I. Gidopoulos and S. Wilson, *this volume*.
25. P. Dutta and S.P. Bhattacharya, *Chem. Phys. Lett.* **162,** 67 (1989).
26. G. Strang, *Linear algebra and its applications*, Academic Press, New York (1976).
27. P.-O. Löwdin, *Phys. Rev.* **139**, A357 (1965).
28. E.A. Hylleraas and B. Undheim, *Z. Phyzik* **65,** 759 (1930).
29. J.K.L. MacDonald, *Phys. Rev.* **43,** 830 (1933).
30. H. Shull and P.-O. Löwdin, *Phys. Rev.* **110**, 1466 (1958).

31. P. Corea De Mello, M. Hehenberger and M.C. Zerner, *Intern. J. Quant. Chem.* **21**, 251 (1982).
32. S. Wilson, *Intern. J. Quant. Chem.* **99**, 925 (2004).
33. V.N. Glushkov and S. Wilson, *Intern. J. Quant. Chem.* **99**, 903 (2004).
34. M.M. Madsen and J.M. Peek, *Atom Data* **2**, 171 (1971).
35. S. Hackel, D. Heinemann, D. Kolb and B. Fricke, *Chem. Phys. Lett.* **206**, 91 (1993).
36. A.O Mitrushenkov, *Chem. Phys. Lett.* **217**, 559 (1994).
37. A.O. Mitrushenkov and Y.Yu. Dmitriev, *Chem. Phys. Lett.* **235**, 410 (1995).