

Short Communication

An eigenvalue problem with orthogonality constraints and its applications to excited state calculations**Received date:** 21-01-2016; **Accepted date:** 23-02-2016; **Published date:** 08-03-2016**CORRESPONDING AUTHOR:** V.N.Glushkov**Address:** Oles Gonchar Dnipropetrovsk National University, Department of Physics, Electronics and Computer Systems, 49010, av. Yu. Gagarin 72, Dnipropetrovsk, Ukraine**E-mail:** v_n_glushkov@yahoo.com**ABSTRACT**

A simple and easily implemented technique for taking orthogonality constraints into account, which has been proposed earlier was used to investigate the effect of the finite dimensional approximation and basis set optimization on the accuracy of excited state energies of the H_2^+ and H_3^{++} molecular ions.

KEY WORDS: Eigenvalue problem, variational principle, orthogonality constraints, basis set optimization**INTRODUCTION**

The development of computational methods that can provide a high accuracy in determining eigenvalues and eigenvectors for a self-conjugate operator H (especially higher one, such as the energies of excited states) is a topical problem. In practice, the exact solution for an eigenvalue problem in an infinite-dimensional Hilbert space of states X is replaced by a solution in a finite-dimensional subspace $M = PX$ with the corresponding projector P , i.e.

$$P(H - E_i)P|\Phi_i\rangle = 0, \quad i = 1, 2, \dots, n, \quad |\Phi_i\rangle = P|\Phi_i\rangle \quad (1)$$

here $n = \dim M$ and the orthoprojector P is defined by a chosen finite basis set.

It is clear that such an approximation reduces the accuracy of calculations. Moreover, a finite subspace which is optimal for the lowest eigenvalue E_1 , in general, does not ensure an acceptable accuracy for the higher eigenvalues. The problem becomes more complex when the constraints (e.g. orthogonality restrictions) are imposed on the eigenvectors:

$$\langle u_s | \Phi_i \rangle = 0, \quad i = 1, 2, \dots, n, \quad (2)$$

$$s = 1, 2, \dots, q < n$$

In general, the constraint vectors $|u_s\rangle \in X$ do not completely belong to subspace M and are arbitrary with respect to the operator PHP . For example, this is a case of the excited state calculations where a basis set specifically designed for the ground state is used to determine the ground state energy and a *different* basis set can be used for excited state calculations.

In the most commonly used approaches for excited states (e.g. [1, 2]) the same basis set is employed for both the ground and excited state even though as long ago as 1958 Shull and Lowdin [3] pointed out "the desirability of using different basis sets for different states". This approach can provide a more compact representation of the accurate excited state wave functions than the use of a common basis set for ground and excited states. Such a scheme requires significant computations and can be justified if there is an efficient method for taking into account constraints of type (2). The conventional methods of constrained optimization (e.g. [4]) proved not to be effective enough to solve the complicated problem of quantum physics.

In this communication a simple and easily implemented asymptotic projection (AP) technique proposed earlier [5-7] for taking orthogonality constraints into account is used to investigate the effect of the finite dimensional approximation and basis set optimization on the accuracy of excited state energies. This communication is arranged as follows: in Section 2, the Rayleigh-Ritz variational

principle with basis set optimization for excited states of the same symmetry as a lower state is described. In Section 3 for the simple systems H_2^+ and H_3^{++} we examine the convergence of the excited state energies with the number of basis functions and the accuracy supported by different scheme for construction of basis sets. One has been shown that basis set optimization provides comparable truncation basis set errors for different states and, thus, leads to an energy difference which deviates from exact one within sub- μ Hartree level of accuracy.

Rayleigh-Ritz variational principle with basis set optimization for excited states

Rayleigh-Ritz variational method is well adapted for the approximate solution of eigenvalue problem (1). In this case the lowest eigenvalue E_1 (the ground state energy) is determined by minimizing the functional

$$E(\Phi) = \langle \Phi | \mathbf{H} | \Phi \rangle / \langle \Phi | \Phi \rangle, \quad |\Phi\rangle = P_1 |\Phi\rangle$$

$$E_1 = E(\Phi_1) = \langle \Phi_1 | \mathbf{H} | \Phi_1 \rangle = \min_{\Phi \in M_1} \langle \Phi | \mathbf{H} | \Phi \rangle / \langle \Phi | \Phi \rangle, \quad \langle \Phi_1 | \Phi_1 \rangle = 1, \quad (1)$$

Here $M_1 \in P_1 X$, P_1 is the orthoprojector defined by a basis set optimized for the ground state, H is Hamiltonian of a system.

The first excited state energy is defined by relation

$$E_2 = E(\Phi_2) = \langle \Phi_2 | \mathbf{H} | \Phi_2 \rangle = \min_{\Phi \in \{\Phi_1\}^\perp} \langle \Phi | \mathbf{H} | \Phi \rangle / \langle \Phi | \Phi \rangle, \quad \langle \Phi_2 | \Phi_2 \rangle = 1, \quad (2)$$

where the minimum is taken over all vectors $|\Phi\rangle$ belonging to the orthogonal complement $\{\Phi_1\}^\perp$ to the vector $|\Phi_1\rangle$, i.e. we deal with optimization subject to the constraint $\langle \Phi | \Phi_1 \rangle = 0$. It should be stressed that $\{\Phi_1\}^\perp \not\subset M_1$, i.e. a subspace $M_2 = P_2 X$ different from M_1 generally can be used for E_2 . Higher eigenvalues are determined in a similar way.

For simplicity we limit ourselves by the first excited state having the same symmetry as the ground one, i.e. a constraint vector $|u\rangle \equiv |\Phi_1\rangle$. To make progress we rewrite the orthogonality constraint in the symmetrical form

$$\langle \Phi | P_u | \Phi \rangle = 0, \quad \text{with } P_u = |\Phi_1\rangle \langle \Phi_1|. \quad (3)$$

Then the stationary condition for the functional $L = \langle \Phi | (\mathbf{H} + \lambda P_u) | \Phi \rangle / \langle \Phi | \Phi \rangle$

and variations $|\delta\Phi\rangle$ in the form

$$|\delta\Phi\rangle = P |\delta\Phi\rangle + \sum_{a=1}^r (\partial_a P) \delta\rho_a \quad (4)$$

lead to equations (see Refs.[6, 7] for more details) from which the energy and a wave function of the first excited state can be determined:

$$P_2 (\mathbf{H} + \lambda P_u) P_2 |\Phi_2\rangle = E_2 |\Phi_2\rangle, \quad |\Phi_2\rangle = P_2 |\Phi_2\rangle$$

The second term in (4) allows the finite dimensional subspace M_2 spanned by the chosen basis set to be rotated within Hilbert space, i.e. non-linear parameters ρ_a of a basis set are optimized directly for a given excited state:

$$\langle \Phi | (\partial_a P_2) (\mathbf{H} + \lambda P_u) | \Phi \rangle = 0, \quad a = 1, 2, \dots, r, \quad \partial_a \equiv \partial / \partial \rho_a$$

In these equations the multiplier is as yet undetermined and condition (3) is not satisfied. The key moment of our AP method is the following statement [6,7]:

The constraint vector $P_2 |\Phi_1\rangle$ tends to an eigenvector of the operator

$$H_{mod} = P_2 (\mathbf{H} + \lambda P_u) P_2 \text{ if and only if } \lambda \Rightarrow \pm\infty.$$

Then the fulfillment of condition (3) will follow automatically due to the orthogonality of the eigenvectors, which correspond to different eigenvalues of a self-conjugate operator. The only addition computation beyond that required for the ground state is evaluation of the overlap matrix element $\langle \Phi_1 | \Phi_2 \rangle$. This result can be easily extended to the higher energy levels. For example, in the case of the second excited state the operator P_u should be substituted by the orthoprojector $P_u = |\Phi_1\rangle \langle \Phi_1| + |\Phi_2\rangle \langle \Phi_2|$.

Applications to the H_2^+ and H_3^{++} molecular ions

In order to assess the effects of basis set truncation on the calculated energies we examined the simple systems H_2^+ and H_3^{++} for which the exact numerical solutions are known [8,9]. Calculations were carried out using the basis sets of 1s-type Gaussian functions, whose non-linear parameters (the orbital exponents and positions of functions) were determined by minimizing the energy for each individual state. We studied both the ground state (GS) and the first excited state (ES) of the same symmetry. For H_2^+ a nuclear separation of 2 bohr was used. For the linear H_3^{++} ion the nuclei were placed at (0,0,0,0,-2,0), (0,0,0,0,0,0) and (0,0,0,0,+2,0).

Fig.1 demonstrates convergence of the energy error $E - E_{exact}$ with the size of the basis set m for the GS (—) and ES (- - -) of the H_2^+ ion. The curves " — " and "- - -" correspond to basis sets

optimized for an individual state whereas "x x x" designates error in the ES energy computed with *basis set optimized for the GS*. A similar situation we observed for H_3^{2+} .

The total energies and vertical excitation energies computed with the largest basis sets (29s functions for H_2^+ and 42s – for H_3^{2+}) are given in Table 1. We observed that the basis set optimization

yields the similar energy contributions from incompleteness of basis sets for both the GS and ES. This leads to high precisional values of excitation energies ΔE (ES -GS) $\sim 0.2\mu\text{Hartree}$. Thus, adjusting basis sets directly to the corresponding states is an important factor for their balanced description.

Figure 1: Energy error for the ground (—) and excited state (---) of H_2^+ as a function of the number functions (m).

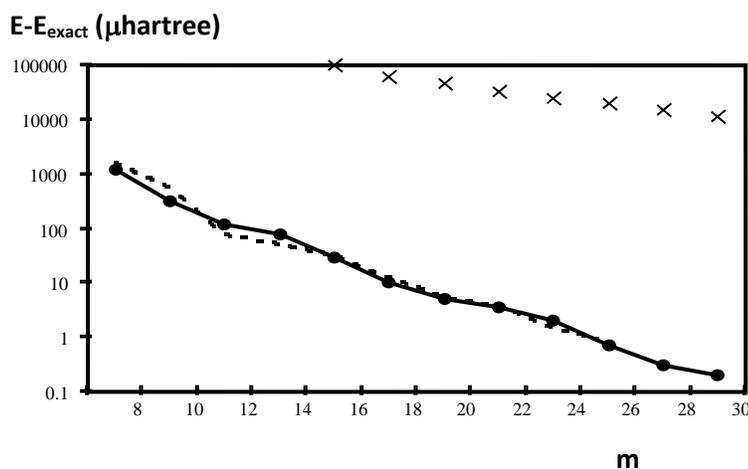


Table 1: Total energies (Hartrees) and error in vertical excitation energies ($\mu\text{Hartrees}$) for H_2^+ and H_3^{2+}

molecule	basis set	E (GS)	E (ES)	ΔE (ES-GS)	$\Delta E_{\text{exact}} - \Delta E$
H_2^+	29s	-0.602 633 99	0.139 135 54	0.741 769 53	0.19
H_3^{2+}	42s	-1.524 159 62	-1.173 373 83	0.350 785 81	0.21

We shall discuss now an accuracy of the fulfillment of the orthogonality constraint as a function of λ . One has been shown that, in general, the constraint vector tends to an eigenvector of the modified operator H_{mod} as $1/\lambda$, so that the limit $\lim_{\lambda \rightarrow \infty} \lambda \langle \Phi_1 | \Phi_2 \rangle$ exists. However, a character of convergence depends on specific features of the particular problem under consideration. In our case of the hydrogen molecular ion Figure 2 shows that the value $\lambda \sim 5 \div 10$ Hartrees ensures the overlap integral value $\langle \Phi_1 | \Phi_2 \rangle < 10^{-7} - 10^{-8}$. As one can see the GS-to-ES transition occurs virtually step-wise within a narrow range of $\lambda \sim 0.74 \div 0.75$ Hartree that corresponds to the excitation energy value (see ΔE from table 1).

In addition we observed that in a wide range $0.75 < \lambda < 10^4$, the value $E_2(\lambda)$ remains almost constant, indicating solution stability ensured by the method.

Thus applying the AP method to the excited state calculations in combination with basis set optimization provides a high accuracy in both the total ES energies and energy difference calculations.

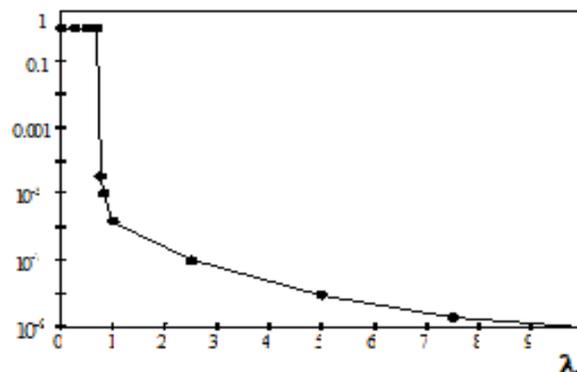


Figure 2: The overlap integral value $\langle \Phi_1 | \Phi_2 \rangle$ as a function of λ for H_2^+ .

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