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Upper and Lower Bounds to Eigenvalues

I. Formalism and Application to H_2^+

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A formalism, based upon Temple's formula, is presented for the determination of the self-consistent orbitals which determine the best upper and lower bounds of an electronic system. The results of use of this method for lower bounds to the H_2^+ ground state are compared to the application of other methods.

Eine Methode, die auf der Formel von Temple beruht, wird angegeben, um diejenigen selbstkonsistenten Orbitale zu erhalten, die die besten oberen und unteren Grenzen eines Elektronensystems bestimmen. Diese Methode wird auf die unteren Grenzen des H_2^+ Grundzustandes angewandt. Die Resultate werden mit denjenigen anderer Methoden verglichen.

Présentation d'un formalisme, basé sur la formule de Temple, pour l'obtention des orbitales self-consistantes qui déterminent les meilleures limites supérieures et inférieures d'un système électronique. Cette méthode est appliquée à la limite inférieure de l'état fondamental de H_2^+ et comparée aux résultats d'autres méthodes.

1. Introduction

A general treatment for excited states within the context of self-consistent orbital theory has been proposed by Fraga and Birss [1]. It is based upon the generalized variational method of Weinstein [8]: an eigenvalue, W, of the Hamiltonian operator, $\underline{H}$, of the system under consideration, may be bracketed according to

$$E - \Delta^{1/2} \leqq W \leqq E + \Delta^{1/2} \tag{1}$$

with

$$E = \langle \Phi | \underline{H} | \Phi \rangle$$
$$\Delta = \langle \underline{H}\Phi | \underline{H}\Phi \rangle - E^2 ,$$

and Φ an approximation to the eigenfunction belonging to the eigenvalue W. In their work, Fraga and Birss chose to vary the trial function, Φ, in order to minimize Δ. In preliminary calculations on the helium atom it has been found that it is difficult to achieve convergence to a chosen state; this is due to the fact that there is no way of explicitly constraining the variational procedure to direct it

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to the given state. The constraint must be implicitly imposed by a judicious choice of the trial function.

An alternative approach is given below which, if it converges at all, converges to a particular chosen state. It is based upon Temple's formula for upper and lower bounds [7] which, in addition to the above feature, gives more accurate estimates for the bounds than the Weinstein formula, using the same approximate trial function.

The Temple formula may be written as

$$B_i = E + \Delta/(E - \tilde{E}_\gamma) \tag{2}$$

where B_i is an upper or lower bound to the exact eigenvalue, W_i, of the Hamiltonian operator, as $\gamma = i-1$ or $i+1$. $\tilde{E}_\gamma$ is an approximation to W_γ. Kato [6] has shown that if the interval $(\tilde{E}_{i-1}, \tilde{E}_{i+1})$ contains only one non-degenerate eigenvalue, and if the inequality

$$\Delta \leqq (E - \tilde{E}_{i-1})(\tilde{E}_{i+1} - E) \tag{3}$$

is satisfied, then upper and lower bounds, B_i^u, B_i^l, exist such that

$$E + \frac{\Delta}{E - \tilde{E}_{i+1}} = B^l \leqq W_i \leqq B^u = E + \frac{\Delta}{E - \tilde{E}_{i-1}}. \tag{4}$$

Eq. (4), hereinafter referred to as the Temple-Kato formula, may be used in conjunction with any trial function which leads to satisfaction of Eq. (3), but of particular interest here are those functions which give the maximum lower bound and minimum upper bound, as distinct from that function which yields the best energy, E.

2. The Self-Consistency Equations

The present work is concerned with the traditional orbital form in which the trial function is written as a Slater determinant consisting of occupied orbitals (or a linear combination of determinants if this is required for satisfaction of angular momentum and symmetry eigenvalue relations.) In this approximation E and Δ are given by,

$$E = 2\sum_{i\lambda\alpha} f_i^\lambda H_i^{\lambda\alpha} + \sum_{i\lambda\alpha}\sum_{m\mu\beta} f_i^\lambda f_m^\mu (2a_{im}^{\lambda\alpha,\mu\beta} J_{im}^{\lambda\alpha,\mu\beta} - b_{im}^{\lambda\alpha,\mu\beta} K_{im}^{\lambda\alpha,\mu\beta}), \tag{5}$$

$$\begin{aligned}\Delta = {} & 2\sum_{i\lambda\alpha} f_i^\lambda X_i^{\lambda\alpha} + \sum_{i\lambda\alpha}\sum_{m\mu\beta} f_i^\lambda f_m^\mu A_{im}^{\lambda\alpha,\mu\beta} \\ & + \sum_{i\lambda\alpha}\sum_{m\mu\beta}\sum_{n\nu\gamma} f_i^\lambda f_m^\mu f_n^\nu B_{imn}^{\lambda\alpha,\mu\beta,\nu\gamma} \\ & + \sum_{i\lambda\alpha}\sum_{m\mu\beta}\sum_{n\nu\gamma}\sum_{p\xi\delta} f_i^\lambda f_m^\mu f_n^\nu f_p^\xi C_{imnp}^{\lambda\alpha,\mu\beta,\nu\gamma,\xi\delta}\end{aligned} \tag{6}$$

using notation and symbols defined in Ref. [1].

The extrema of Eq. (2) with respect to variation in the orbitals, $\phi_i^{\lambda\alpha}$, are obtained by setting the variation in B to zero, subject to the constraints of orthonormality

among the orbitals of a given symmetry, here taken to be $\lambda\alpha$. One has,

$$\delta B = \delta E + \frac{\delta \Delta}{E - \tilde{E}} - \frac{\Delta\, \delta E}{(E - \tilde{E}_\gamma)^2} = 0\,, \tag{7}$$

which yields

$$\delta E + \omega' \, \delta \Delta = 0 \tag{8}$$

with

$$\omega' = \frac{E - \tilde{E}_\gamma}{(E - E_\gamma)^2 - \Delta}\,. \tag{9}$$

The trial function which, under variation, satisfies Eq. (8) will serve as the function to obtain the best bound when used in Eq. (2). In particular, assume that one is interested in obtaining upper and lower bounds to the eigenvalue of the k^{th} state. For the upper bound of the k^{th} state one would need $\tilde{E}_{k-1}$, an approximation to the eigenvalue of the $(k-1)^{\text{th}}$ state. With $\tilde{E}_{k-1}$ and a Φ, one would use Eq. (8) to determine the $\Phi_k^{\min}$, which gives the best upper bound to W_k. The Φ which satisfies Eq. (8) in this case, $\Phi_k^{\min}$, must be such as to yield the minimum value of Eq. (2).

For the lower bound one would use $\tilde{E}_{k+1}$ and determine by use of Eq. (8) the $\Phi_k^{\max}$ which would yield the best lower bound. This function would yield the best lower bound obtainable from a function of type Φ, when it was substituted into Eq. (2).

Thus, so long as one knows an $\tilde{E}_{k+1}$ and an $\tilde{E}_{k-1}$, one is insured by Kato's theorem that when Eq. (2) is used one will determine bounds to the k^{th} state; Eq. (8) also guarantees that the bounds are the best obtainable from a function of the form Φ. It should be noted that from Kato's theorem the inequality $\Delta < (E - \tilde{E}_{k-1})\,(\tilde{E}_{k+1} - E)$ must be satisfied. This does not however imply that Δ must bracket W_k, i.e., $E - \sqrt{\Delta} \leqq W_k \leqq E + \sqrt{\Delta}$, as seems to have assumed in the literature in the past [2–4]. On the contrary, Δ as determined by a $\Phi_k^{\max}$ may be such that $E - \sqrt{\Delta} < W_{k+1} < E + \sqrt{\Delta}$, and yet this Δ and $\Phi_k^{\max}$ will serve to give a lower bound to the k^{th} state. The only restriction on Δ is that it must satisfy the inequality given in Kato's theorem.

For the purposes of Eq. (8), δE and $\delta \Delta$ are given as functions of the variations, $\delta \phi_i^{\lambda\alpha}$, in the orbital, $\phi_i^{\lambda\alpha}$, of symmetry designation $\lambda\alpha$,

$$\delta E = 2 \sum_{i\lambda\alpha} \left\{ \langle \delta \phi_i^{\lambda\alpha} | f_i^\lambda \left[2\underline{H}' + \sum_{m\mu\beta} f_m^\mu \underline{I}_m^{\mu\beta} \right] | \phi_i^{\lambda\alpha} \rangle + \text{complex conjugate} \right\}, \tag{10}$$

$$\begin{aligned} \delta \Delta = \sum_{i\lambda\alpha} \Big\{ \langle \delta \phi_i^{\lambda\alpha} | f_i^\lambda \Big[& 2\underline{X} + \sum_{m\mu\beta} f_m^\mu \underline{A}_m^{\mu\beta} \\ & + \sum_{m\mu\beta} \sum_{n\nu\gamma} f_m^\mu f_n^\nu \underline{B}_{mn}^{\mu\beta,\nu\gamma} \\ & + \sum_{m\mu\beta} \sum_{n\nu\gamma} \sum_{p\xi\delta} f_m^\mu f_n^\nu f_p^\xi \underline{C}_{mnp}^{\mu\beta,\nu\gamma,\xi\delta} \Big] | \phi_i^{\lambda\alpha} \\ & + \text{complex conjugate} \Big\} \end{aligned} \tag{11}$$

with the notation and symbols of Ref. [1].

The orthonormality conditions give rise to the variational constraints,

$$\langle \phi_i^{\lambda\alpha} | \phi_j^{\lambda\alpha} \rangle = \delta_{ij}\,.$$

Using the method of undetermined multipliers, with $-\theta_{ji}^{\lambda\alpha}$ the multipler for the i,j^{th} constraint, the totality of terms to be added to Eq. (8) is

$$-\sum_{i\lambda\alpha}\sum_{j\lambda\alpha}[\theta_{ji}^{\lambda\alpha}\langle\delta\phi_i^{\lambda\alpha}|\phi_j^{\lambda\alpha}\rangle+\theta_{ij}^{\lambda\alpha}\langle\delta\phi_j^{\lambda\alpha}|\phi_i^{\lambda\alpha}\rangle]. \tag{12}$$

Addition of Eqs. (8) and (12) leads to, after some manipulation,

$$\sum_{i\lambda\alpha}\left\{\left\langle\delta\phi_i^{\lambda\alpha}|\underline{F}_i^{\lambda\alpha}\phi_i^{\lambda\alpha}-\sum_j\theta_{ji}^{\lambda\alpha}\phi_j^{\lambda\alpha}\right\rangle+\text{complex conjugate}\right\}=0 \tag{13}$$

where

$$\begin{aligned}\underline{F}_i^{\lambda\alpha}=f_i^{\lambda}\Big\{&2(\underline{H}'+\omega'\underline{X})+\sum_{m\mu\beta}f_m^{\mu}(\underline{N}_m^{\mu\beta}+\omega'\underline{A}_m^{\mu\beta})\\&+\sum_{m\mu\beta}\sum_{n\nu\gamma}f_m^{\mu}f_n^{\nu}\omega'\underline{B}_{mn}^{\mu\beta,\nu\gamma}\\&+\sum_{m\mu\beta}\sum_{n\nu\gamma}\sum_{p\xi\delta}f_m^{\mu}f_n^{\nu}f_p^{\xi}\omega'\underline{C}_{mnp}^{\mu\beta,\nu\gamma,\xi\delta}\Big\}.\end{aligned} \tag{14}$$

Since Eq. (13) holds for any arbitrary infinitesimal variations $\delta\phi_i^{\lambda\alpha},\delta\bar{\phi}_i^{\lambda\alpha}$, it follows that

$$\underline{F}_i^{\lambda\alpha}\phi_i^{\lambda\alpha}=\sum_j\phi_j^{\lambda\alpha}\theta_{ji}^{\lambda\alpha} \tag{15}$$

with a similar equation involving $\bar{\phi}_i^{\lambda\alpha}$, $\bar{\theta}_{ji}^{\lambda\alpha}$. Since the Lagrangian multipliers are elements of an Hermitian matrix, the equations are equivalent.

In the general open-shell system, the coupling operator defined by Fraga and Birss [1] can now be employed to transform Eq. (15) to a pseudo-eigenvalue equation,

$$\underline{R}^{\lambda\alpha}\phi_i^{\lambda\alpha}=\theta_{ii}^{\lambda\alpha}\phi_i^{\lambda\alpha}. \tag{16}$$

In closed-shell systems, with all $\underline{F}_i^{\lambda\alpha}$ equal, the orbitals may be subjected to a linear transformation which leaves the $\underline{F}$ operator invariant and produces a diagonal matrix of Lagrangian multipliers and the pseudo-eigenvalue equation,

$$\underline{F}\,\phi_i^{\lambda\alpha}=\theta_{ii}^{\lambda\alpha}\phi_i^{\lambda\alpha}. \tag{17}$$

3. Application to H_2^+

In applying this formalism the most practical method is to expand the orbitals in some suitable basis set, $\chi_p^{\lambda\alpha}$,

$$\phi_i^{\lambda\alpha}=\sum_p c_{ip}^{\lambda}\chi_p^{\lambda\alpha}.$$

Eqs. (16) and (17) can then be expressed in terms of the linear coefficients, c_{ip}^{λ}, and the matrix representations of the $\underline{R}^{\lambda\alpha}$ or $\underline{F}$ operators under the basis set. The procedure is then the familiar one of any iterative self-consistency approach, with the solutions of the pseudo-eigenvalue equations being used to construct the operators (or their matrix representations), until self-consistency is attained. The resultant orbitals are then used to calculate E_i, the approximate eigenvalue of the Hamiltonian operator, and the bound, Eq. (2).

It should be noted that the procedure must be carried out independently for the upper and lower bound to a given state, using the appropriate $\tilde{E}_\gamma$. In the iterative procedure, with M occupied orbitals of symmetry $\lambda\alpha$, this requires using the highest M eigenvectors in forming the operator consistent with the lower bound, and the lowest M eigenvectors when dealing with the upper bound.

The method has been applied to the ground state of the hydrogen molecule ion. Since the upper bound is best determined by the variational method for lowest states, only the lower bound is considered here. The trial function used is a generalization of the James function [5],

$$\phi = e^{-\alpha\xi} \sum_i c_i \eta^{2i}$$

where ξ and η are the variables in the confocal elliptic coordinate system. The integrals were evaluated using, in part, the analytical forms of Goodisman and Secrest [3].

Table 1. *Lower bounds, in Hartree units, for the* H_2^+ *system*

Expansion length	I	II	III
2	−1.10388	−1.10403	−1.10706
		−1.13797	−1.14724
4	−1.10286	−1.10303	
		−1.12509	

Exact eigenvalue at 2 a.u. internuclear distance is −1.10263 Hartrees.

Table 1 gives the lower bounds determined by: I. the method of this paper; II. minimization of Δ, according to Ref. [1]; III. Goodisman and Secrest. The latter calculation was based on two terms of Eq. (18), and a two dimensional grid over α and c_1/c_0. Where required, the value of $\tilde{E}_1$ was taken as −0.36087, the exact eigenvalue for the first excited state of Σ_g^+ symmetry at 2 a.u. internuclear separation.

In II and III the function was obtained by minimization of Δ. Subsequent substitution of this value, and the corresponding approximate energy, into the Temple formula gave the upper of the pairs of values appearing in Table 1. The lower of the pairs is that obtained from the Weinstein formula. The results of II

Table 2. *Comparison of lower bounds*

No. Basis functions	Δ	Bound	α	Variational scheme
2	0.001422	−1.10430	1.355	E
2	0.001444	−1.10388	1.320	B
3	0.000903	−1.10367	1.355	E
3	0.000790	−1.10286	1.310	B
5	0.000915	−1.10286	1.310	E
5	0.000790	−1.10286	1.310	B

and III differ because in II the coefficients were determined automatically; these do not, except coincidentally, fall on the grid chosen in III.

The bounds obtained by the method developed here (variational scheme B) and those obtained by using the function which minimizes the energy in the Temple-Kato formula (variational scheme E) are compared in Table 2.

As expected, the bound determined by the present method based upon Temple's formula is consistently the best. Further, the use of the function obtained by Δ minimization (II, Table 1) or by E minimization (scheme E, Table 2) in the Temple formula does not achieve nearly as good a result as the *a priori* use of the method developed in this paper, emphasizing the need to distinguish the quantity varied to obtain the function.

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