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Variational-Bound Method for Autoionization States*

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A variational method which provides upper bounds to energies of atomic autoionization states (QHQ eigenvalues) without requiring knowledge of target eigenstates is sought. For two-electron atoms, it is found that such a method is provided by a superposition of configurations of a single set of arbitrarily chosen orbitals, with a (physically plausible) prescribed choice of secular-equation roots. This conclusion is applicable to calculations of Holstien, and explains the observed "stabilization of roots."

The states of interest herein are subject to autoionization within the nonrelativistic approximation, being associated with resonances in electron-atom scattering.¹ Many of the resonances are quite narrow and it is natural to attempt to calculate these quasidecrete compound-atom² states by methods similar to those which are commonly used to calculate true discrete states. The Rayleigh-Ritz method when applied to discrete states has the desirable properties of providing energy bounds and being subject to indefinite extension so as to provide as good an approximation as desired. The variational theorem^{3,4} guarantees that the i th lowest root of the secular equation is an upper bound to the energy of the i th lowest state which is not orthogonal to the trial function by symmetry. This theorem does not apply in a straightforward way to compound-atom autoionization states, which lie above an infinite number of states of the same symmetry; this limitation was formally overcome by O'Malley and Geltman,² as noted below. The variational theorem does apply to states such as the $4S^e$ and $4P^o$ states of Li below the lowest $3S$ state of Li⁺; these are true discrete states within the nonrelativistic approximation, even though they lie above the Li ionization threshold.⁵

Following O'Malley and Geltman,² we define autoionization states as eigenfunctions of QHQ , where $P = 1 - Q$ is the Feshbach projection opera-

tor which projects onto the energetically accessible target eigenstates. For two-electron atoms, and energies below the lowest inelastic threshold, we have

$$Q = Q_1 Q_2 = Q_2 Q_1, \quad (1)$$

$$Q_i = 1 - P_i, \quad (2)$$

$$P_i = |u_0(\vec{r}_i)\rangle\langle u_0(\vec{r}_i)|. \quad (3)$$

For two-electron atoms an alternative, but equivalent, definition is that autoionization states are those states corresponding to stationary-energy functions in Q space, the space of quadratically integrable functions which have identically vanishing overlap with the wave function(s) of the lower-lying state(s) of the target. It seems plausible to assume that this alternative definition is also meaningful and appropriate for systems with more than two electrons. It is interesting to note that this definition also encompasses such states as the quartet states of Li referred to above, since the vanishing overlap is immediately assured by symmetry properties.

The eigenvalues of QHQ , as distinguished from those of H itself, are discrete in the energy range of interest; hence the Rayleigh-Ritz method is at least formally applicable and the variational theorem guarantees energy bounds. O'Malley and Geltman showed that one can deal variationally

with H rather than QHQ provided the trial function is first operated on by Q . Thus we have that

$$\langle Q\Phi_s | H | Q\Phi_s \rangle = \epsilon_s \langle Q\Phi_s | Q\Phi_s \rangle. \quad (4)$$

These authors² calculated a number of autoionization states of He and H^- by Rayleigh-Ritz expansions, each term of which was obtained by operating with the explicitly-constructed Q operator on an initially arbitrary expansion term. An approach which avoids construction of the Q operator is to initially construct the trial function so that it lies in Q space. Each of these approaches requires use of knowledge of the target wave function(s); we seek a method which provides energy bounds while avoiding this requirement altogether. Such a method would seem desirable for two-electron autoionization states, and would be even more useful if it can be extended to more complicated cases. For targets containing more than one electron, it is not a trivial matter to construct functions lying in Q space even if the target functions are assumed known, and there is the further complication that the exact target wave functions are not known.

We consider the calculation of autoionization states in two-electron atoms by use of a spatial trial function $\psi_{\text{tr}}(\vec{r}_1, \vec{r}_2)$. In order that this function lie in Q space, it must satisfy the Q constraints

$$\int u_n^*(\vec{r}_1) \psi_{\text{tr}}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 = 0, \quad (5)$$

$$\int u_n^*(\vec{r}_2) \psi_{\text{tr}}(\vec{r}_1, \vec{r}_2) d\vec{r}_2 = 0, \quad (6)$$

where n ranges from 1 through n_{max} , corresponding to all energetically accessible target states. For autoionization states below the $2s$ threshold, $n_{\text{max}} = 1$. For states between the $2s$ and $3s$ thresholds, $n_{\text{max}} = 5$, corresponding to $1s$, $2s$, and triply-degenerate $2p$ target eigenstates. We introduce a set of M linearly independent symmetry orbitals $v_i(\vec{r})$ which are orthogonal to certain of the target eigenfunctions $u_n(\vec{r})$,

$$\int u_n^*(\vec{r}) v_i(\vec{r}) d\vec{r} = 0, \quad \text{for } n < i, \\ n = 1 \text{ through } n_{\text{max}}, \quad (7)$$

but are otherwise arbitrary. We can form an orbital-product expansion (OPE) trial function which lies in Q space by taking products of such of the $v_i(\vec{r})$ as are orthogonal to target eigenstates below the threshold of interest, i. e., by putting

$$\psi_{\text{tr}}(\vec{r}_1, \vec{r}_2) \\ = \sum_{i=n_{\text{max}}+1}^M \sum_{j=n_{\text{max}}+1}^M C_{ij} v_i(\vec{r}_1) v_j(\vec{r}_2). \quad (8)$$

A particularly simple choice for the $v_i(\vec{r})$ is just the target eigenfunctions; this choice was successfully employed by Altick and Moore.⁶ Restriction to this special form for the $v_i(\vec{r})$ might, however, produce some limitations on over-all convergence, as it is known to do when dealing with discrete states.⁷ Without making this special choice, it should be feasible to perform calculations with the $v_i(\vec{r})$ chosen for best convergence, subject only to the constraints (7). Note that the $v_i(\vec{r})$ are allowed to overlap continuum target eigenstates. We have performed in this way trivial calculations based on a single-term trial function. It is interesting to note that the calculations of O'Malley and Geltman² can be viewed as an example of this method, with each of the initially arbitrary orbitals made orthogonal to the target ground state by admixture of appropriate multiples of the target ground-state function itself. Of course their calculations can also be viewed as involving explicit introduction of the Q operator. Bhatia *et al.*⁸ used the Q operator and nonseparable trial-function terms, which cannot be viewed as an example of (7) and (8).

As an alternative to (8), one might employ an expansion containing some orbitals $v_i(\vec{r})$ which are not orthogonal to lower-lying target states, e. g.,

$$\psi_{\text{tr}}(\vec{r}_1, \vec{r}_2) = \sum_{i=1}^M \sum_{j=1}^M C_{ij} v_i(\vec{r}_1) v_j(\vec{r}_2). \quad (9)$$

The variational theorem guarantees that the $K+1$ th lowest root of the secular equation of (9) lies above the l th lowest root of the secular equation of (8), and hence above the energy of the l th lowest autoionization state. Here K is just the number of additional terms in (9) as compared with (8) which are introduced as a result of modifying the lower summation limits. For the OPE itself, the value of K is obvious. In practice it is convenient to use, instead of the OPE itself, a superposition of configurations (SC) consisting of combinations of expansion terms which couple to the desired over-all symmetry. When working with a SC it is necessary to take into account, in evaluating K , the fact that certain orbital products may not enter at all for certain symmetries; e. g., $v_1(\vec{r}_1) v_1(\vec{r}_2)$ does not enter when calculating 3S states. From the present point of view, there is no advantage in actually using (9) rather than (8). Lipsky and Russek⁹ have, however, quite successfully calculated autoionization states of He with SC equivalent to (9), the $v_i(\vec{r})$ being chosen as target eigenstates. They justify the elimination of low-lying secular-equation roots on the grounds that these are approximating to physical bound states. Temkin¹ has pointed out that such a justification could not be applied to similar calculations of autoionization states in H^- . We have just

seen that the elimination of these low-lying roots is justified by the variational theorem, and hence upper bounds to QHQ eigenvalues will result.

When the $v_i(\vec{r})$ are chosen as target eigenstates, it appears that the use of (9), as compared with (8), leads to only slightly higher (poorer from present point of view) values in the case of He,⁹ but considerably higher values for H⁻.¹

All the methods described above require use of knowledge of target eigenstate(s). We next derive a method which avoids this requirement. We consider an OPE, or equivalent SC, of the same general form as (9) but with the linearly-independent symmetry orbitals $\varphi_i(\vec{r})$ not required to satisfy orthogonality constraints such as (7), and put

$$\psi_{\text{tr}}''(\vec{r}_1, \vec{r}_2) = \sum_{i=1}^M \sum_{j=1}^M C_{ij}'' \varphi_i(\vec{r}_1) \varphi_j(\vec{r}_2). \quad (10)$$

Now we may form linear combinations of the $\varphi_i(\vec{r})$ in such a way as to obtain a set of $v_k(\vec{r})$ which satisfy (7). Thus we put

$$v_k(\vec{r}) = \sum_{i=1}^M T_{ki} \varphi_i(\vec{r}); \quad k = 1 \text{ through } M. \quad (11)$$

It is possible to find this transformation, since the number of transformation parameters, T_{ki} , exceeds the number of constraints (7). It follows that (10) is equivalent to (9), with

$$C_{ij}'' = \sum_{k=1}^M \sum_{l=1}^M T_{ki} T_{lj} C_{kl}'. \quad (12)$$

Thus we may apply to the OPE (10), or an equivalent SC, the conclusion arrived at with respect to (9), namely that the $K+l$ th lowest secular-equation root is an upper bound to energy of the l th lowest autoionization state of the chosen symmetry. For convenience of discussion we may apply the qualitative designations 1s, 2s, 2p, etc., to either the orbitals $v_i(\vec{r})$ or $\varphi_i(\vec{r})$, but it must be borne in mind that the $\varphi_i(\vec{r})$ which is designated by 2s is not necessarily orthogonal to the target ground state. For this reason, the value of K for a SC equivalent to (10) must be essentially determined from the full expansion (10); e.g., in calculating a ¹S autoionization state, one cannot justifiably reduce the value of K by unity by merely omitting from the expansion (10) a term qualitatively designated by 1s2s.

In summary, upper-bound estimates of energies of two-electron autoionization states (QHQ eigenvalues) of a preselected symmetry may be obtained by taking the (physically plausible) prescribed root of the secular equation of a SC based on a single, arbitrarily chosen, set of orbitals. It is not necessary to make use of knowledge of lower-lying target state(s) in this procedure, notwithstanding the fact that the very definition of these states is based on the target state(s).

This is analogous to the fact that ordinary excited states may be defined as corresponding to stationary-energy functions in the space of functions which are orthogonal to the lower-lying states of the desired symmetry, and yet upper-bound energy estimates can be obtained by the Rayleigh-Ritz procedure without introducing wave functions of lower states. In each case, the avoidance of introduction of other wave functions in the computational procedure can be understood in terms of the maximum-minimum property of eigenvalues.¹⁰⁻¹² This property was explicitly used in a previous derivation of the autoionization-state method described above.¹²

The property of providing autoionization-state energy bounds does not apply to a completely general SC calculation, but applies to the present method as a result of the two requirements that (1) all configurations in a particular calculation must be formed from a single (though arbitrary) set of orbitals, and (2) the secular-equation root corresponding to particular state must be chosen in a prescribed manner. Although the requirement (1) is not always satisfied in SC calculations of ordinary discrete states, it does not seem to be a very severe or unreasonable limitation. Such a requirement has considerable heuristic appeal, being consistent with the notion of forming the configurations from the eigenfunctions of a one-electron operator. At the same time, it is not required that the orbitals be eigenfunctions of a special one-electron operator, such as the Hartree-Fock operator, which might result in poor convergence.

The prescribed choice of K which enters into requirement (2) is mathematically founded and does not depend on qualitative arguments regarding large and small components,¹ insensitivity to variation of a scale factor,¹³ or insensitivity to extension of the basis.⁹ The value of K can be determined by the physically plausible process of listing *all* configurations which can be formed from the given set of orbitals (labeled in the usual order) and counting those in which one or both electrons are insufficiently excited. For definiteness we list some values of K for calculations of ¹S autoionization states below the 2s threshold. Using orbitals (1s, 2s, 2p), one can form four ¹S configurations; 1s², 1s2s, 2s², and 2p². For this four-term expansion $K=2$, corresponding to elimination of secular-equation roots associated with the first two of these configurations. With orbitals (1s, 2s, 2p, 3s, 3p, 3d) or (1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f) we may form 10- or 20-term expansions, for which the corresponding values of K are 3 and 4. The 10- and 20-term expansions also provide bounds to energies of ¹S autoionization states between the 2s and 3s thresholds, the corresponding values of K being 7 and 10, respectively. The inclusion of all orbitals consistent with a given maximum value of the

principal quantum number in the qualitative orbital designation is a rather natural choice, but is not essential. One is, for example, free to delete or add orbitals with $l \neq 0$ when treating S states below the $2s$ threshold, without the value of K being affected, since such orbitals satisfy the constraint (7) by angular properties.

Some existing calculations can be interpreted as examples of the proposed method for two-electron atoms. The calculations of Lipsky and Russek⁹ are one example, but not a very interesting one for the present purposes in view of the special choice of orbitals. More interesting examples are given by the rather extensive calculations of Holøien,¹³ who used Laguerre functions as orbitals, with a common exponential parameter for all orbitals. Although his choice of secular-equation roots was based on different considerations, it was, for a number of calculations (e.g., 4-, 10-, and 20-term expansions noted above) the same as prescribed herein; the cor-

responding results lie slightly above the best available estimates of QHQ eigenvalues, as we would expect. To test the plausible assumption that such expansions in the limit will converge to the exact QHQ eigenvalues for two-electron systems, further extensive calculations are in progress by Holøien.¹⁴ The expansions will be made more flexible by introducing more than one exponential parameter in some of the basis functions. It should be noted that the very successful earlier calculations of Holøien were carried out long before development of the Q -operator formalism, and were pioneering efforts based on physical insight. The stabilization of roots which he noted in those calculations seems to be understandable through the present derivation which arises from the Q -operator formalism.

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