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Bounds on Energy Levels and Lifetimes of Auto-Ionizing States*

A. Russek, H. C. Wu, and J. Owens
Department of Physics, University of Connecticut, Storrs, Connecticut

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Upper and lower bounds on the energy level of an auto-ionizing state are derived by a method which is a generalization of the Stevenson-Crawford formula for the lower bound on the ground state of a system. These bounds are nonvariational in character, although the lower bound can be used together with a variational upper bound to obtain a narrower gap between upper and lower bound. In addition, an upper bound on the transition rate for the decay of the auto-ionizing state is derived. Although primarily designed to yield information for more than two-electron systems, for which the Hahn, O'Malley, and Spruch version of the Feshbach projection operators cannot explicitly be written down, the methods are here applied to auto-ionizing states in helium below the $n=2$ threshold. These bounds are found to be a far more sensitive test of the adequacy of an approximate state than is the conventional energy criterion used in conjunction with the variational approach.

I. INTRODUCTION

In recent years auto-ionizing states of the two-electron systems He and H^- have been extensively studied. The most successful treatment has been in terms of the Feshbach projection operator formalism.[1] In this formalism, an auto-ionizing state of an atom described by the Hamiltonian H can be defined to be an eigenstate of QHQ (which is also written as H_{QQ}), where Q is a Feshbach projection operator defined below by[2-4]

$$QHQ(Q\psi)=E(Q\psi). \tag{1}$$

The definition (1) is not unique, inasmuch as the projection operator Q is not unique. There are infinitely many projection operators which satisfy the Feshbach requirement on Q; namely that it exclude any state which has the asymptotic behavior of the ionized state. (This is not a very precise statement, but it will be made more precise in Sec. III.) Two distinct Q operators have so far been introduced in the treatment of auto-ionizing states in helium below the $n=2$ limit. Hahn, O'Malley, and Spruch[5] define Q space to include all functions in which neither electron has any component of the $1s$ hydrogenic state with $Z=2$. On the other hand, Lipsky and Russek[3] define Q space to be that space spanned by a finite basis set of bound-state hydrogenic product states which may or may not include any $1s$ component with $Z=2$. Altick and Moore[4] use a similar Q space except that they further omit $1s$ hydrogenic states, so that their Q space is a subspace of that defined by Hahn, O'Malley, and Spruch. (Clearly, there are as many different Q operators as there are different basis sets.) It might be mentioned in passing that although O'Malley and Geltman[2] and Bhatia, Temkin, and Perkins[6] use the projection operators defined by Hahn, O'Malley, and Spruch, their results are limited by the dimensions of the respective trial function spaces used in the variational calculations. And it is simple to show that their variational wave functions and energies are exactly equivalent to the solution of Eq. (1) for a Q space which is the intersection of the variational trial function space used with the Q space of Hahn, O'Malley, and Spruch.

Despite the fact that Q space, and consequently E, is not uniquely determined by the asymptotic requirements imposed on Q, the location of the resonance energy E_{res} for any given scattering process is in fact unique[2]:

$$E_{\text{res}}=E+\Delta. \tag{2}$$

Thus the physics of the situation is unaffected by the arbitrariness inherent in the definition of Q. The quantity denoted by Δ and called the "level shift" makes up for any inaccuracy due to those basis functions left out of Q space and also incorporates any real shift in the precise locations of resonances which arise from different types of scattering phenomena (e.g., e^- on He^+, or $h\nu$ on He, etc.). This point will be discussed in greater detail in Sec. III.

Now, the theoretical situation insofar as it pertains to helium below the $n=2$ threshold is quite satisfactory. Several different approaches have all yielded substantially the same set of auto-ionizing energy levels and these are in good agreement with experiment. In retrospect it is clear that the Q operator of Hahn, O'Malley, and Spruch is, for this case, superior to that used by Lipsky and Russek. Besides being much larger in dimension than the latter, the former also provides variational upper bounds which the latter does not, unless $1s$ states are excluded from the basis product set as was done by Altick and Moore.

However, the situation changes when other, more complicated, systems are considered. For example, when a $2p$ electron is ejected from argon by an x-ray photon, the resulting Ar^+ ion is in a highly excited auto-ionizing state, in the order of 200 eV above its ground state. It will decay with the emission of one or several electrons by an Auger or multiple Auger transition. In this case, an infinite number of states of Ar^{++}, Ar^{++}, etc., must be excluded from Q space in the Hahn, O'Malley, and Spruch definition. Furthermore, not a single one of these states can be expressed exactly (they are all many-body eigenfunctions) in order to construct a projection operator that will project these states out of Q space.

On the other hand, a finite basis set of configurations of product independent-particle model states can readily be formed to serve as a basis for Q space. As a matter of fact, Auger transitions have long been calculated with a Q space consisting of only a single basis element, namely a Hartree or Hartree-Fock state for the initial ion wave function. What has been lacking heretofore is a test for the adequacy of the basis set used to define Q space.

The main purpose of the present paper will be to demonstrate the existence of bounds, both upper and lower, that can be derived to bracket the auto-ionizing energy level and test for the adequacy of the basis set used to define Q space. These bounds are *not* variational in nature. They are variants of the Stevenson-Crawford formula for the lower bound on the ground state as applied to higher states.[7] Moreover, it will be seen that a lower bound on the lifetime of the auto-ionizing state can also be obtained.

II. FORMULATION OF THE BOUNDS

In this section we will formulate and prove an inequality from which it will be possible to derive both upper and lower bounds on the energy of an auto-ionizing state and to obtain a lower bound to the lifetime of that state. First, however, the motivation for so doing will be presented.

As pointed out in the Introduction, it is possible only in the simplest cases to actually construct the projection operators we would like to use. In all other cases, it is necessary to make do with a rather small dimensional Q space in order to obtain any results at all. And even in the case of helium, where the desired projection operators can actually be constructed, the variational approach subsequently used limits the effective Q space used to the dimension of that part of function space included in the trial function. One goal of the inequality to be demonstrated below is to permit the bracketing, both above and below, of the energy of an auto-ionizing state which would follow from a Q space we would like to use in terms of the Q space we are able to handle.

To this end, we first decompose Hilbert space into two disjoint parts by a pair of complementary projection operators P and Q:

$$P^2 = P, \quad Q^2 = Q, \quad PQ = 0, \quad P + Q = 1 . \tag{3}$$

Here, Q space is that which we would like to use were it feasible. Since we will not in general be so fortunate, we further partition Q space into two disjoint parts, one of which we are able to handle. Thus

$$Q = Q_T + R , \tag{4}$$

where Q_T space, which we call trial-function space, is such that the eigenvalues and eigenfunctions of $Q_T H Q_T$ can be solved for exactly:

$$Q_T H Q_T \,|\, Q_T \psi\rangle = \mathcal{E}_T \,|\, Q_T \psi\rangle \ . \tag{5}$$

Since Q_T and R are themselves projection operators, we have, in addition to (4),

$$Q_T{}^2 = Q_T , \quad R^2 = R, \quad Q_T R = 0 , \tag{6a}$$

and, of course, $PQ_T = PR = 0$. (6b)

An elementary example of such a decomposition can be found in the case of helium below the $n = 2$ limit. Here Q would be the Q operator of Hahn, O'Malley, and Spruch which contains all functions of $\vec{r}_1$ and $\vec{r}_2$ in which neither electron has any $1s$ hydrogenic component with $Z = 2$:

$$\begin{aligned} Q = 1 - |\,\phi_0(1)\rangle_1\langle\phi_0(1)| - |\,\phi_0(2)\rangle_2 \\ \times\langle\phi_0(2)| + |\,\phi_0(1)\phi_0(2)\rangle\langle\phi_0(1)\phi_0(2)| , \end{aligned} \tag{7}$$

where ϕ_0 is the hydrogenic $1s$ state with $Z = 2$,

$$\phi_0(i) = (8/\pi)^{\frac{1}{2}}\, e^{-2r_i} \ . \tag{8}$$

The subscript 1 or 2 between the brackets indicates that the inner product is to be taken over that variable only. On the other hand, Q_T space could be some finite basis set of configurations of hydrogenic product states which contained no ϕ_0 component, as was used by Altick and Moore,

$$Q_T = \sum_{n=1}^{N} |U_n(1,2)\rangle\langle U_n(1,2)| \ , \tag{9}$$

where U_n is a properly symmetrized (for singlet states) or antisymmetrized (for triplet states) configuration of hydrogenic product states. Thus n stands for the set of quantum numbers L, M_L, n_1, l_1, n_2, l_2. Alternatively, Q_T space could be a finite basis set of Hylleraas functions with $\phi_0(1)$ and $\phi_0(2)$ projected out as was used by Bhatia, Temkin, and Perkins. In either choice, Q_T space is a finite dimensional subspace of Q space and, in both cases, the eigenfunctions and eigenvalues of Q_THQ_T are known exactly.

In other, more complicated cases, such as argon with a vacancy in the $2p$ shell, Q_T space might consist of a single basis element, such as the appropriate Hartree-Fock product state. It will be seen that it is not actually necessary to construct the full Q space in order to make use of the inequality to obtain the bounds.

A. Bounds on the Energy

The inequality will now be stated and will be proved below. Let ϕ_T and $\mathcal{E}_T$ be an eigenfunction and eigenvalue of Q_THQ_T

$$Q_THQ_T\phi_T=\mathcal{E}_T\phi_T, \tag{10}$$

$$\text{where}\quad Q_T\phi_T=\phi_T,\quad R\phi_T=P\phi_T=0. \tag{11}$$

Then there exists an eigenfunction ψ of QHQ belonging to the energy eigenvalue E:

$$QHQ\psi=E\psi, \tag{12}$$

such that E lies between the bounds

$$\mathcal{E}_T-\sigma^{1/2}\leqslant E\leqslant\mathcal{E}_T+\sigma^{1/2}, \tag{13}$$

where σ is defined to be

$$\begin{aligned}\sigma(\mathcal{E}_T)&=\langle\phi_T|(H-\mathcal{E}_T)^2|\phi_T\rangle\\&=\langle(H-\mathcal{E}_T)\phi_T|(H-\mathcal{E}_T)\phi_T\rangle\geqslant 0.\end{aligned} \tag{14}$$

It is clear from (14) that σ, being the inner product of some quantity with itself, is greater than or equal to zero. It is equal to zero, if, and only if, ϕ_T is a true eigenfunction of H. In that case, of course, E will be equal to $\mathcal{E}_T$.

In proving the inequality stated by Eqs. (12)–(14), it is convenient first to decompose the non-negative definite quantity σ into two non-negative definite parts. Using the completeness property of (3), i.e., $P+Q=1$, it is possible to rewrite σ as

$$\begin{aligned}\sigma(\mathcal{E}_T)&=\langle\phi_T|(H-\mathcal{E}_T)(P+Q)(H-\mathcal{E}_T)|\phi_T\rangle\\&=\langle\phi_T|(H-\mathcal{E}_T)P(H-\mathcal{E}_T)|\phi_T\rangle\\&\quad+\langle\phi_T|(H-\mathcal{E}_T)Q(H-\mathcal{E}_T)|\phi_T\rangle\\&\equiv\sigma_P(\mathcal{E}_T)+\sigma_Q(\mathcal{E}_T).\end{aligned} \tag{15}$$

Further, using the idempotency properties of P and Q expressed by Eqs. (3) and the fact that P and Q are Hermitian, we can rewrite σ_P and σ_Q so as to show their non-negative definite character:

$$\sigma_P=\langle P(H-\mathcal{E}_T)\phi_T|P(H-\mathcal{E}_T)\phi_T\rangle, \tag{16a}$$

$$\sigma_Q=\langle Q(H-\mathcal{E}_T)\phi_T|Q(H-\mathcal{E}_T)\phi_T\rangle. \tag{16b}$$

As a consequence of (15) and (16) we have two important inequalities which will be used in the proof below.

$$\sigma(\mathcal{E}_T)\geqslant\sigma_P(\mathcal{E}_T)\geqslant 0, \tag{17a}$$

$$\sigma(\mathcal{E}_T)\geqslant\sigma_Q(\mathcal{E}_T)\geqslant 0. \tag{17b}$$

The importance of Eqs. (17) stems from the fact that, in the general case, we are not able to construct P and Q and, therefore cannot actually calculate σ_P or σ_Q. Equations (17), however, provide us with an upper bound to both. Using (11), we can further rewrite σ_Q as

$$\sigma_Q=\langle Q(H-\mathcal{E}_T)Q\phi_T|Q(H-\mathcal{E}_T)Q\phi_T\rangle. \tag{18}$$

To proceed with the proof of the inequality expressed by Eqs. (12)–(14), we expand the trial function ϕ_T in terms of the eigenfunctions ψ_n of QHQ which are assumed to form a complete orthonormal set which spans Q space,

$$Q=\textstyle\sum_n|\psi_n\rangle\langle\psi_n|. \tag{19a}$$

$$\text{where}\quad QHQ\psi_n=E_n\psi_n. \tag{19b}$$

The summation over n stands for summation over the discrete portion of the spectrum and integration over the continuous portion. Remembering that ϕ_T, which lies in Q_T space, is automatically an element of Q space, we can expand ϕ_T in terms of the ψ_n:

$$\phi_T=\textstyle\sum_n a_n\psi_n. \tag{20a}$$

$$\text{where}\quad \textstyle\sum_n|a_n|^2=1. \tag{20b}$$

Substituting the expansion (20) into the expression (18) for σ_Q, we get, after using (19b) and the orthonormality properties of the ψ_n,

$$\sigma_Q=\textstyle\sum_n|a_n|^2(E_n-\mathcal{E}_T)^2. \tag{21}$$

Now, of the entire set of eigenvalues E_n of QHQ, there must be one, say E_m, which lies closest in value to the trial energy $\mathcal{E}_T$. (We exclude from consideration the case in which $\mathcal{E}_T$ lies equally close to two levels E_m and E_{m+1}. Except for degeneracies, i.e., $E_m=E_{m+1}$, the unlikelihood of such an occurrence is such that the case does not warrant detailed treatment, and degeneracies will have been removed at the outset by restriction to a particular symmetry state, e.g., ^1P.) Thus we have

$$(E_n - \mathcal{E}_T)^2 \geq (E_m - \mathcal{E}_T)^2 . \tag{22}$$

Using this, we have immediately that

$$\sigma_Q(\mathcal{E}_T) \geq (E_m - \mathcal{E}_T)^2 \sum_n |a_n|^2 = (E_m - \mathcal{E}_T)^2 . \tag{23}$$

As a corollary to this result, in those cases for which we are either not able or willing to construct QHQ, we have that

$$\sigma(\mathcal{E}_T) \geq \sigma_Q(\mathcal{E}_T) \geq (E_m - \mathcal{E}_T)^2 . \tag{24}$$

Finally, taking square roots of one of the inequalities contained in (24) we get

$$\sigma_Q^{1/2} \geq |E_m - \mathcal{E}_T| , \tag{25}$$

or, in more usable form,

Theorem I: $\mathcal{E}_T - \sigma_Q^{1/2} \leq E_m \leq \mathcal{E}_T + \sigma_Q^{1/2}$. (26)

Similarly, from the other inequality expressed in (24) we get the weaker, but often more usable result,

Theorem II: $\mathcal{E}_T - \sigma^{1/2} \leq E_m \leq \mathcal{E}_T + \sigma^{1/2}$. (27)

We note that the bounds on an auto-ionizing level established by Eq. (26) or Eq. (27) are not variational in nature. They can be used even with the Q_T space employed by Lipsky and Russek where the Hylleraas-Undheim theorem yields no useful information. It may, however, be the case, as with the Q_T space used by Altick and Moore or Bhatia, Temkin, and Perkins, that useful information on upper bounds can be obtained from the Hylleraas-Undheim theorem. In that case, the lower bound provided by (26) or (27) can be combined with the upper bound supplied by the Hylleraas-Undheim theorem, in the following theorem:

If for a set of levels E_n where $0 \leq n \leq N$ the trial function energies $\mathcal{E}_n$ from the eigenstates of $Q_T H Q_T$ are each closer to the corresponding energy level E_n than to any other E_s, i.e.,

$$|\mathcal{E}_n - E_n| \leq |\mathcal{E}_n - E_s|, \quad \text{for } s \neq n, 0 \leq n \leq N, \tag{28}$$

then the energies E_n are bracketed by

Theorem III: $\mathcal{E}_n - \sigma_Q^{1/2} \leq E_n \leq \mathcal{E}_n$, (29)

and

Theorem IV: $\mathcal{E}_n - \sigma^{1/2} \leq E_n \leq \mathcal{E}_n$. (30)

It should be noted that Eq. (29) is a simple extension of the Stevenson-Crawford formula for a lower bound on the ground state where the Hamiltonian under consideration is QHQ. Theorems III and IV can also be applied to excited nonauto-ionizing states (i.e., the ordinary optically excited states) by simply setting $Q = 1$, since, in this case, there is no unbound state to

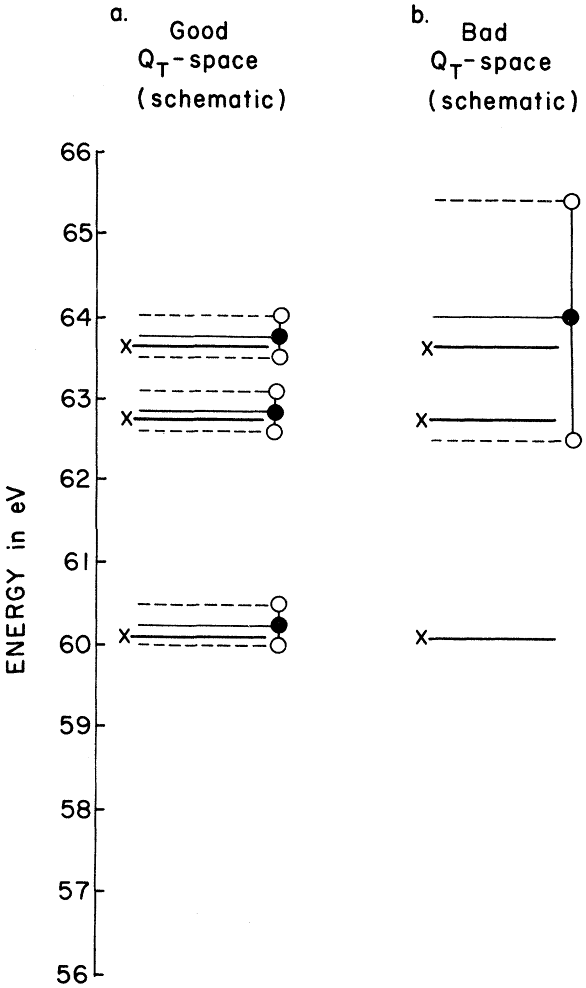

FIG. 1. The energy-level diagram shown in Part a schematically depicts an ideal case. The crosses show the true levels, the solid circles show the eigenvalues $\mathcal{E}_T$ of $Q_T H Q_T$, and the open circles, together with the vertical lines, show the upper and lower bounds $\mathcal{E}_T \pm \sigma^{1/2}$. It is stressed that these are not actual calculations, but merely indicate what could be obtained with a good trial function space Q_T. Part b schematically depicts a poor case. This too does not represent an actual calculation, but is designed to show what could happen with a very poor Q_T space. In particular, it illustrates how the upper and lower bounds can indeed bracket an energy level, as required by Theorems I and II and yet not provide a lower bound to the lowest energy level.

project out, so that $P=0$. Of course Theorems III and IV become identical in this case.

Figure 1a indicates schematically the ideal situation when the conditions (28) apply and trial function space Q_T is good. Figure 1b indicates schematically what could happen, however, were one to choose deliberately or by extreme misfortune a very poor basis to define Q_T space. Figure 2 shows the actual results obtained for the first-three ${}^1P$ and the first-three ${}^3P$ auto-ionizing states for helium using an eight function basis of product hydrogenic states of the type suggested by Altick and Moore. These results will be discussed at greater length in Sec. IV.

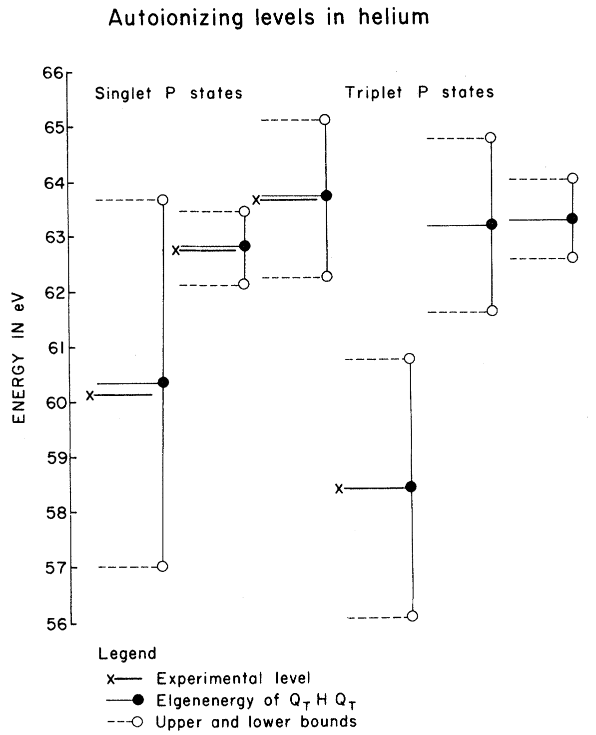

FIG. 2. The results of an actual calculation using as a basis for Q_T space the eight-state hydrogenic product configurations listed in Sec. IV. The crosses show the experimental levels, the solid circles show the eigenvalues of $Q_T H Q_T$, and the open circles, together with the vertical lines show the upper and lower bounds $\mathcal{E}_T \pm \sigma^{1/2}$. It is seen that in actual calculations, even with a relatively poor basis set, the conditions for the applicability of Theorems III and IV are satisfied. It is also seen here that the σ bounds provide a far more sensitive test than does the energy criterion. The levels shown here are the lowest three states in the odd singlet P series and in the odd triplet P series.

Finally, we note that the weaker theorem on bounds, Theorem II, does not involve Q space at all. This is fortunate, on the one hand, because it permits us to obtain bounds on the energy E even when it is not feasible to write down the Q operator explicitly. However, we are led to question whether the theorem breaks down if Q space is extended in size beyond that which is appropriate to define the auto-ionizing levels of the atom in question. The answer to that question is negative. The theorem remains valid, but the relevance of the eigenenergies of QHQ to the auto-ionizing levels breaks down. Were the dimensionality of Q space indefinitely extended so that $Q\rightarrow 1$ and $P\rightarrow 0$, more and more eigenenergies of QHQ would appear in any given energy interval. As a consequence, it would become trivially true that at least one eigenenergy of QHQ would lie in an energy interval of $2\sigma^{1/2}$ centered about the eigenenergy $\mathcal{E}_T$ of $Q_T HQ_T$. In the limit $Q=1$ there would be a continuous number of eigenenergies of QHQ in this interval. Thus it is clear that the theorem does not help us to define a good Q space. It only gives us information about the eigenenergies of QHQ if we have a Q_T space which is a subspace of an acceptable Q space. The problem of how, in principle, to define a good Q space in the general case is deferred to Sec. III.

B. Bound on the Lifetime

We now turn our attention to σ_P which will supply us with an upper bound on the transition rate, corresponding to a lower bound on the lifetime of an auto-ionizing state. In order to make the physics more apparent, we will first restrict ourselves to the simplest case of a single open channel, such as helium below the $n=2$ threshold, despite the fact that the primary aim of this paper is to provide a means for handling more complicated cases.

Since P, being a linear operator, commutes with any constant, and since ϕ_T lies in Q space [see Eq. (11)], we have

$$P\mathcal{E}_T\phi_T=\mathcal{E}_T P\phi_T=0. \tag{31}$$

Using this result, σ_P, as defined by Eq. (16a) becomes

$$\sigma_P=\langle PH\phi_T | PH\phi_T\rangle=\langle\phi_T | HPH | \phi_T\rangle . \tag{32}$$

We shall use σ_P, as given by Eq. (32), to establish an upper bound on the transition rate Γ. To facilitate this, it is convenient to introduce, by analogy with Eqs. (19), a particular orthonormal basis set which spans P space; namely, the eigenfunctions of PHP.

$$PHP|v_k\rangle=E_k|v_k\rangle , \tag{33a}$$

where the normalization conditions (remembering that the eigenspectrum of PHP is partly discrete and partly continuous) are taken to be

$$\begin{aligned}\langle v_k | v_{k'} \rangle &= \delta_{k,k'}, && \text{discrete portion,}\\ &= \delta(E_k - E_{k'}), && \text{continuous portion. (33b)}\end{aligned}$$

Taken together, the eigenstates $|v_k\rangle$ of PHP plus the eigenstates $|\psi_n\rangle$ of QHQ form a complete orthonormal basis set for the entire Hilbert space. We will use this set to express both σ_P and the transition rate, Γ, so that they may more readily be compared.

Decomposing the Hamiltonian H into two parts,

$$H = H_0 + H', \quad H_0 = PHP + QHQ, \quad H' = PHQ + QHP, \tag{34}$$

it is seen that the eigenstates $|v_k\rangle$ and $|\psi_n\rangle$ are also eigenstates of H_0. Thus, for example,

$$\begin{aligned}H_0|v_k\rangle &= PHP|v_k\rangle + QHQ|v_k\rangle\\ &= E_k|v_k\rangle + 0 = E_k|v_k\rangle\ .\end{aligned}$$

The set $|\psi_n\rangle$ contains the auto-ionizing states, while the set $|v_k\rangle$ contains the continuum into which the former decay. Thus we regard the auto-ionizing state $|\psi_n\rangle$ as an eigenstate of H_0 created at time $t = 0$, which subsequently decays into a packet of continuum eigenstates $|v_k\rangle$ of H_0 through the interaction term H'. For the case at hand, with the normalization (33b), the transition probability per unit time, Γ, is given, by first-order time-dependent perturbation theory,[8] as

$$\Gamma = (2\pi/\hbar)|\langle v_K | H' | \psi_N \rangle|^2, \tag{35}$$

where conservation of energy requires that $E_K = E_N$.

We now turn our attention to σ_P. Using the fact that the set $|v_k\rangle$ forms a basis set for P space, we may write

$$P = \textstyle\sum_k |v_k\rangle\langle v_k| + \int dE_k |v_k\rangle\langle v_k|, \tag{36}$$

where we sum over the discrete portion of the spectrum and integrate over the continuous portion of the spectrum. Substituting (36) into (32), we obtain

$$\begin{aligned}\sigma_P &= (\textstyle\sum_k + \int dE_k)|\langle v_k | H | \phi_T \rangle|^2\\ &= (\textstyle\sum_k + \int dE_k)|\langle v_k | PHQ | \phi_T \rangle|^2\\ &= (\textstyle\sum_k + \int dE_k)|\langle v_k | H' | \phi_T \rangle|^2 .\end{aligned} \tag{37}$$

Remembering that ϕ_T is an approximation to the auto-ionizing state which we have labeled by ψ_N (by definition, it is the best approximation we have available, since Q_T space is the largest subspace of Q space for which we are able to obtain the eigenstates), we will replace ϕ_T in (37) by ψ_N:

$$\sigma_P \simeq (\textstyle\sum_k + \int dE_k)|\langle v_k | H' | \psi_N \rangle|^2 . \tag{38}$$

If now we plot $|\langle v_k | H' | \psi_N \rangle|^2$ as ordinate versus E_k as abscissa, as is done in Fig. 3a, we see from Eq. (38) that σ_P is merely the area under the curve, provided we assign a rectangle with unit base to each point in the discrete spectrum. On the other hand, we see from Eq. (35) that $\hbar\Gamma/2\pi$ is just the height of the curve at abscissa E_K. Although there is no connection in general between the area under a non-negative curve and the height of the curve at a particular value of abscissa, there is a connection in this particular case, as is shown schematically in Figs. 3a and b and demonstrated below. The important consideration in this connection is that *if* the decay from the initial state ψ_N to the ionized state is to follow the exponential decay law, $\exp(-\Gamma t)$, then the very derivation of Eq. (35) from time dependent perturbation theory requires that the quantity $|\langle v_k | H' | \psi_N \rangle|^2$ must remain essentially constant over an energy range which is no smaller than $\hbar\Gamma/2$ on either side of the energy $E_k = E_K$. (This will insure at least a recognizable portion of the Lorentzian line shape which is associated with the

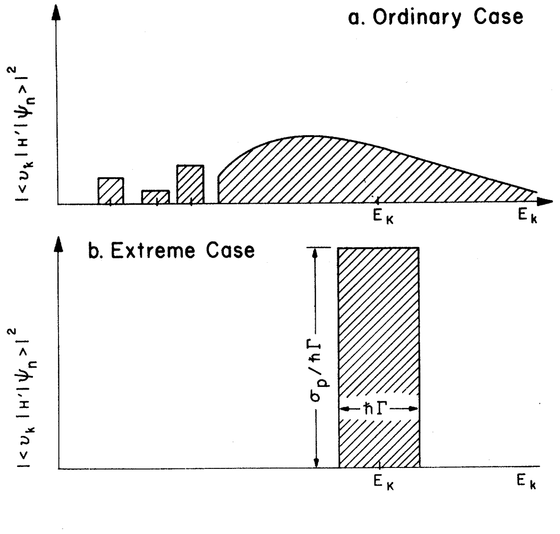

FIG. 3. Part a shows a schematic plot of $|\langle v_k | H' | \psi_n \rangle|^2$ as a function of E_k as would ordinarily be expected. Unit base is here assigned to each discrete level. Part b shows a schematic plot of $|\langle v_k | H' | \psi_n \rangle|^2$ as a function of E_k with the same value of σ_P (i.e., area) as Part a but for the extreme case for which only those continuum functions are in P space which are in a narrow energy band around E_K.

exponential decay in time. Actually, the matrix element should not change appreciably over a much broader energy range if the exponential time behavior is to persist over several decades.) Under this restriction, the largest value that the ordinate $|\langle v_K|H'|\psi_N\rangle|^2$ can attain will occur when the entire area represented by σ_P is located in the interval $\hbar\Gamma$ around E_K, while maintaining the ordinate constant in this interval as required by the argument above. This extreme case, of course, produces a rectangle with base $\hbar\Gamma$. This is illustrated in Fig. 3b. The area in 3b is equal to the area in 3a, i.e., σ_P is the same for both. However, by concentrating it all in the interval $\hbar\Gamma$ around E_K we have maximized the height. (Note that in this Figure $\hbar\Gamma$ has been taken to be unduly large to make the point more transparent.) This extreme case can, in principle, be achieved by placing unwanted states $|v_{\tilde{i}}\rangle$ in Q space, as will be discussed in Sec. III below.

Since the extreme case represented by Fig. 3b need not (and will, in general, not) apply for a given Q space, the ordinate $|\langle v_K|H'|\psi_N\rangle|^2$ satisfies the inequality

$$\hbar\Gamma|\langle v_K|H'|\psi_N\rangle|^2 \leq \sigma_P . \tag{39}$$

It follows, after elimination of $|\langle v_K|H'|\psi_N\rangle|^2$ in Eq. (39) and Eq. (35), and recalling Eq. (17a), that

$$\sigma \geq \sigma_P \geq \hbar\Gamma(\hbar\Gamma/2\pi) = \hbar^2\Gamma^2/2\pi . \tag{40}$$

It must be stressed that the result (40) is *not* a proof. It is valid only so long as Q space is properly chosen so that auto-ionizing states do indeed decay to the ionized state according to the exponential decay law. Although this property is customarily assumed without question, the point is here being made that until it is rigorously justified it remains an assumption. The most that can be rigorously claimed, taking into account also that ψ_N has been substituted for ϕ_T, is the following:

Theorem V: If the auto-ionizing state under consideration does decay exponentially in time with a decay rate $\exp(-\Gamma t)$, then an upper bound to a quantity $\tilde{\Gamma}$ exists and is given by

$$\tilde{\Gamma} \leq (2\pi\sigma_P)^{1/2}/\hbar \leq (2\pi\sigma)^{1/2}/\hbar , \tag{41}$$

where $\tilde{\Gamma}$ is the approximate transition rate that would ordinarily be calculated in first-order time-dependent perturbation theory using the best available approximation to the initial state.

Although Theorem V has so far been demonstrated only for a single open channel, the theorem is true even if the auto-ionizing state can decay through many channels, as will be proven shortly. Theorem V appears to be a highly watered down assertion. Nevertheless, it yields a good deal of information about the outcome of calculations as they are actually done in practice. In practice one never really has an exact expression for either the initial or final state. One calculates the transition rate with approximations to each. Theorem V yields an upper bound to the transition rate that would be obtained with the best approximation available to the initial state (which ϕ_T is, by definition) and with the correct final state. Thus it is seen that the theorem is, in reality, a useful result.

It now remains to extend the validity of Theorem V to the more complicated cases which are the primary concern of this work. The vast majority of auto-ionizing states encountered in practice are energetically able to decay via several channels, not just one as in the very specially selected case of helium below the $n=2$ threshold. To take a very simple example of the more complicated case, one need only consider auto-ionizing states of helium below the $n=3$ threshold. After decay, the residual ion can be in the $1s$, the $2s$, or the $2p$ states. The outgoing electron will carry off the appropriate energy and angular momentum required to conserve these quantities. Thus there are, in this energy range, three disjoint continua or "channels" into which the auto-ionizing state can decay. The final states now have to be labeled not only by the energy continuum of the outgoing electron, but also by the quantum numbers describing the particular channel. These quantum numbers will be denoted by α. Each channel has its own independent transition rate, Γ_α, and, with the normalization adopted for the continuum states, unit density of final states. Thus

$$\Gamma_\alpha = (2\pi/\hbar)|\langle v_{\alpha,K_\alpha}|H'|\psi_N\rangle|^2 . \tag{42}$$

The total transition rate Γ is given by the sum of the individual channel rates,

$$\Gamma = \sum_\alpha \Gamma_\alpha , \tag{43}$$

since the various final states are all mutually orthogonal, and the probabilities (which $\Gamma_\alpha dt$ represent) are additive. Clearly Eqs. (42) and (43) are general and hold for arbitrary number of open channels.

As in the discussion before Eq. (39), the derivation of Eq. (42) from time-dependent perturbation theory requires that the matrix element for each channel α does not vary appreciably over the energy range $\hbar\Gamma$. (It must be remembered that the lifetime of the auto-ionizing state and, consequently, the energy width, is determined by the over-all Γ.) Consequently, σ_P, which is now a sum of integrals, one for each channel, yields the upper bound

$$\sigma_P \geq \sum \hbar \Gamma \, |\langle v_{\alpha, K_\alpha} | H' | \psi_N \rangle|^2 . \tag{44}$$

Remembering again that $\sigma \geq \sigma_P$, and substituting for the absolute value square of the matrix element from Eq. (42), we have, with the help of (43),

$$\sigma \geq \sigma_P \geq \sum_\alpha (\hbar \Gamma)(\hbar \Gamma_\alpha / 2\pi) = \hbar^2 \Gamma^2 / 2\pi , \tag{45a}$$

$$\text{or} \quad \Gamma \leq (2\pi \sigma_P)^{1/2} / \hbar \leq (2\pi\sigma)^{1/2}/\hbar . \tag{45b}$$

Thus Theorem V has been demonstrated even for those auto-ionizing states which can decay through many channels. This case, as has been pointed out, is at once more common in practice and more difficult to treat theoretically.

III. DEFINITION OF AUTO-IONIZING STATES

The work in the preceding section has all been predicated on the existence of an adequate Q space of which the trial function space, Q_T space, is a subspace. This is a relatively simple task in the case of helium, for which the projection operators are easily constructed. For more complicated systems, however, this is not true. Only Q_T space can be constructed. This section will therefore be devoted to the definition, in principle, of the optimum Q space for a given auto-ionizing state.

Before proceeding with this task, though, a question of semantics must first be settled. It has been noted, in the Introduction, that the actual location of a given resonance in a given scattering process is independent of the particular set of Feshbach projection operators used to treat the scattering process. The discrepancy between the true location of the resonance and the eigenenergy of QHQ is corrected by the level shift Δ. However, it must not be assumed that the precise location of the resonance energy will be the same for all collision processes (e.g., e^- on He^+, $h\nu$ on He, etc.). Consequently, in this work an auto-ionizing state of energy E will be *defined* to be the eigenstate of QHQ, where the projection operator Q is the one which projects into the maximal subspace of Hilbert space which excludes only the true ionized states at energy E, i.e., the continuum states into which the auto-ionizing state actually decays. This definition will be discussed in detail below. It must, however, be stressed that this is not a practical definition from the standpoint of computational convenience. It is an in principal definition designed to permit further mathematical development. It must also be stressed that, semantically, this is just a definition; the precise location of all resonances in any scattering experiment will still require a level shift, Δ. However, this level shift will presumably be very small. It will correct only for the small differences in the exact locations of resonances for different scattering processes, and not for inadequacies in the basis set used to define Q space.

In the above definition it will be noted that allowance is made for the fact that the auto-ionizing level will, in general, be degenerate with many true ionized states, not just one as in the case of helium below the $n = 2$ limit. It must also be noted that the Q operators are only implicitly defined by the above definition. Before one can remove from Hilbert space all ionized states at energy E, one must know the value of E and the line width of the state under consideration. Clearly, a different maximal Q space is required for each auto-ionizing level. The best Q space that can be constructed to yield a set of auto-ionizing states is the intersection of the separate Q spaces associated with each of the states in the set. Thus it is obvious that if a maximal Q space is desired that will yield an entire set of auto-ionizing levels, it is smaller than the maximal Q space for any individual level in the set and will therefore give somewhat poorer results. In practice, even smaller Q_T spaces are used which remove all ionized states over a broad range of energies which is certain to include E (and, in the case of a finite basis set, much more) in order to obtain usable projection operators.

The starting point in the definition of Q space is the selection of Q_T space, which, for the sake of simplicity, we will take to be a single dimensional subspace of function space. This one-dimensional subspace is denoted by ϕ_T. In practice, ϕ_T will probably be selected as one of the solutions of a multidimensional diagonalization or variational procedure, but this is not necessary. Since Q_T space is one dimensional, we must clearly have

$$Q_T H Q_T \phi_T = \mathcal{E}_T \phi_T , \tag{46a}$$

$$\text{where} \quad \mathcal{E}_T = \langle \phi_T | Q_T H Q_T | \phi_T \rangle = \langle \phi_T | H | \phi_T \rangle . \tag{46b}$$

The complementary space, denoted by P_0, must somehow be decomposed into two disjoint subspaces, P space and R space:

$$P_0 \equiv 1 - Q_T = P + R . \tag{47}$$

This will be done by an iteration process. We first find the eigenfunctions and eigenvalues of

$$(1 - Q_T) H (1 - Q_T) = P_0 H P_0 .$$

This can in principle be done because the operators H and Q_T are both known. By (47) these eigenfunctions span the combined space $P+R$. From this basis set, all those which belong to eigenvalues of P_0HP_0 within an interval

$$\delta E=[1+\tfrac{1}{2}(2\pi)^{1/2}]\sigma^{1/2} \tag{48}$$

on either side of $\mathcal{E}_T$ are placed in P_1 space; all the remaining eigenfunctions are placed in R_1 space. Thus v_ϵ is in P_1 space, i.e.,

$$P_1v_\epsilon=v_\epsilon,\quad Q_Tv_\epsilon=R_1v_\epsilon=0, \tag{49a}$$

$$\text{if}\quad P_0HP_0v_\epsilon=\epsilon v_\epsilon\ , \tag{49b}$$

$$\text{where}\quad \mathcal{E}_T-\delta E\leqslant\epsilon\leqslant\mathcal{E}_T+\delta E\ . \tag{49c}$$

Here δE is a quantity which we know, by Theorems II and V, to be larger than the difference between the exact energy E and the trial energy $\mathcal{E}_T$ plus the half-width of this state. As a consequence, the ionized state has definitely been included in P_1 space.

Here σ, by the same reasoning as that used to derive Eqs. (15) and (16), is given by

$$\sigma=\sigma(Q_T)+\sigma(P_0)\ , \tag{50a}$$

where

$$\sigma(Q_T)=\langle Q_T(H-\mathcal{E}_T)Q_T\phi_T\,|\,Q_T(H-\mathcal{E}_T)Q_T\phi_T\rangle\equiv0\ , \tag{50b}$$

because $Q_T\phi_T$ is an eigenstate of Q_THQ_T. We now define

$$Q_1=Q_T+R_1\ , \tag{50c}$$

which, together with P_1 as defined by (49), constitute a complementary pair of projection operators satisfying the conditions expressed by Eqs. (3). The subscripts 1 on these operators signify that Q_1 is not the maximal Q space for the autoionizing state under consideration, but only the first iteration in the process, Q_T being the zeroth iteration.

It will be proven in the Appendix that the eigenspectrum of Q_1HQ_1 has the same "window" in the continuous part of the spectrum as does R_1HR_1, and has one, and only one, discrete level in the energy range

$$\mathcal{E}_T-\delta E\leqslant E\leqslant\mathcal{E}_T+\delta E\ .$$

This energy eigenspectrum is illustrated in Fig. 4 along with the eigenspectra of the other operators that are pertinent to the discussion.

If we now denote by $\mathcal{E}_1$ the energy, and by ϕ_1 the state function, of the single discrete level of Q_1HQ_1 in the energy range

$$\mathcal{E}_T-\delta E\leqslant E\leqslant\mathcal{E}_T+\delta E$$

(these are the first iterated corrections to the original trial values), we may begin the process all over again, treating $\mathcal{E}_1$ and ϕ_1 as we previously treated $\mathcal{E}_T$ and ϕ_T. The one important difference is that σ will now be much smaller, because P_1 space is a subspace of P_0 space by (47). This can be seen from Eq. (37); as we remove states from P space, we reduce $\sigma(P)$ with each state removed. This will make δE smaller in the next iteration, and further reduce P space by subdividing P_1 space into P_2+R_2, etc.,

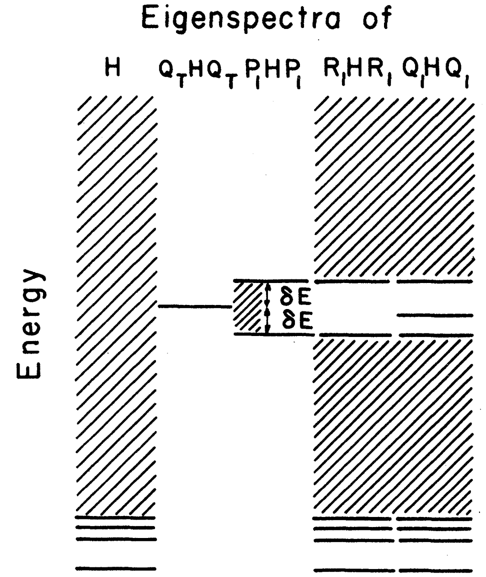

FIG. 4. Eigenspectra of several operators of interest.

$$\sigma(P_0)>\sigma(P_1)>\sigma(P_2)>\cdots>\sigma(P_n)\ , \tag{52a}$$

$$\text{so that}\quad \delta E_0>\delta E_1>\delta E_2>\cdots>\delta E_n\ . \tag{52b}$$

The iteration process just described must not, however, make δE arbitrarily small, because in insisting that the ionized state must always be in P space, we must not reduce P space beyond the point where the equality holds in Eq. (45a). Let us say that this occurs at the nth iteration:

$$\sigma(P_n)=\hbar^2\Gamma^2/2\pi\ . \tag{53a}$$

But

$$\Gamma=\textstyle\sum_\alpha\Gamma_\alpha$$

$$=(2\pi/\hbar)\textstyle\sum_\alpha|\langle v_{\alpha,K_\alpha}|P_nHQ_n|\phi_N\rangle|^2 \tag{53b}$$

so that

$$\sigma(P_n)=2\pi(\textstyle\sum|\langle v_{\alpha,K_\alpha}|P_nHQ_n|\phi_N\rangle|^2)^2\ . \tag{53c}$$

It should be noted that even the first iteration, Q_1, is larger than the Q space of Hahn, O'Malley, and Spruch. This is so because Q_1 includes product states not only of the form $|\,1s,np\rangle$, but also $|\,1s,kp\rangle$ for all k outside of a relatively narrow energy band. The significance of the Q space of Hahn, O'Malley, and Spruch can be ascertained by recalling that an acceptable Q space for several auto-ionizing states is the intersection of the acceptable Q space for the individual states. It is therefore clear that the Q space of Hahn, O'Malley, and Spruch is only the largest Q space that will yield *all* auto-ionizing states of helium below the $n=2$ threshold without advance knowledge of the precise locations of these levels.

IV. NUMERICAL RESULTS

To summarize the content of the last section, we have demonstrated that it is possible, in principle, to define a Q space such that if ϕ is an eigenstate of QHQ, then the equalities hold in Eq. (45a):

$$\sigma=\sigma_P=\hbar^2\Gamma^2/2\pi \quad .$$

In actual practice, of course, the iteration procedure outlined therein cannot be carried out. However, the theorems of Sec. II do provide a criterion to discriminate between the quality of alternative trial function spaces that have been proposed, with a test that is far more sensitive than is the lowest energy criterion of the usual variational test. This is illustrated very clearly by the results presented below, using as trial function space, Q_T, an eight-dimensional subspace of the Q space of Hahn, O'Malley, and Spruch, spanned by the eight hydrogenic product configurations listed in Table I. These configurations are the only significant contributors, from the 55-state basis of Ref. 3, to the three lowest odd parity singlet and triplet auto-ionizing P states.

Table II lists the matrix elements of r_{12}^{-1} and r_{12}^{-2} needed to calculate σ. Starting from Eq. (14) and using the fact that

$$\mathcal{E}_T=\langle\phi_T|Q_THQ_T|\phi_T\rangle=\langle\phi_T|H|\phi_T\rangle \quad ,$$

σ can be simplified to

$$\sigma=\langle\phi_T|H^2|\phi_T\rangle-\langle\phi_T|H|\phi_T\rangle^2 \quad .$$

Writing $\phi_T=\sum_\alpha a_\alpha\psi_\alpha$ (where the listing presented in Table I is employed),

$$\begin{aligned}\langle\phi_T|H^2|\phi_T\rangle &=\textstyle\sum_\alpha a_\alpha^{\,2}(e_\alpha^{\,2}+2e_\alpha V_{\alpha\alpha}+(V^2)_{\alpha\alpha})\\ &\quad+2\textstyle\sum_{\alpha>\beta}a_\alpha a_\beta[(e_\alpha+e_\beta)V_{\alpha\beta}+(V^2)_{\alpha\beta}] \quad ,\\ \langle\phi_T|H|\phi_T\rangle &=\textstyle\sum_\alpha a_\alpha^{\,2}(e_\alpha+V_{\alpha\alpha})\\ &\quad+2\textstyle\sum_{\alpha>\beta}a_\alpha a_\beta V_{\alpha\beta} \quad ,\end{aligned}$$

where $e_{n,n'}=-2[n^{-2}+(n')^{-2}]$,

and $(V^p)_{\alpha\beta}=\langle\psi_\alpha|r_{12}^{\;-p}|\psi_\beta\rangle$.

These are just the energies of the hydrogenic product configurations and the matrix elements listed in Table II. Finally, Table III lists the coefficients a_α for each of the states, and the value of σ in a.u.^{2} for each state.

TABLE I. Ordering of the states. The quantum number π denotes singlet states and triplet states.

$\psi_1^{(\pi)}=(2s,2p)^\pi P$
$\psi_2^{(\pi)}=(2s,3p)^\pi P$
$\psi_3^{(\pi)}=(3s,2p)^\pi P$
$\psi_4^{(\pi)}=(2s,4p)^\pi P$
$\psi_5^{(\pi)}=(4s,2p)^\pi P$
$\psi_6^{(\pi)}=(2p,3d)^\pi P$
$\psi_7^{(\pi)}=(2p,4d)^\pi P$
$\psi_8^{(\pi)}=(2p,5d)^\pi P$

Also listed in Table III, for convenience, is the value of $\sigma^{1/2}$ in eV. These results are plotted in Fig. 2. The crosses show the experimental values, while the closed circles show the theoretical values obtained for the energies, using this eight-dimensional Q_T space. As is already well known, the eigenenergies of Q_THQ_T are in excellent agreement with the experimental results for those states which have so far been excited experimentally. (Transitions to ^3P states are forbidden for photon absorption and are less likely than ^1P states for electron impact, so that only the first member in the triplet series has so far been measured.)

Clearly, with such good agreement in energies, using even a small basis set, the energy discrepancies do not furnish a sensitive criterion for evaluating the quality of a given trial function space. On the other hand, the quantities $\mathcal{E}_T\pm\sigma^{1/2}$ (where $\sigma^{1/2}$ is taken from Table III) are represented, for each state, by the open circles. It is seen that $\sigma^{1/2}$ varies from ~ 0.67 to ~ 3.3 eV. This is to be compared with values of 5.6×10^{-5} eV to 0.017 eV for $\hbar\Gamma/(2\pi)^{1/2}$ which follow from the results of Burke and McVicar[9] for these two cases, respectively. It is seen that the $\sigma^{1/2}$ index to the quality of these approximations to the respective auto-ionizing states happily leaves room for improvement by factors of 200 to 10^4. This improvement must ultimately come from a better choice of the correlations at small interelectron separations which must be included in the wave functions. These are, of course, very poorly represented by small sets of products of bound-state hydrogenic orbitals. To achieve correlations at small interelectron separations, packets of continuum hydrogenic states must also be included. These high-energy components con-

TABLE II. Matrix elements of r_{12}^{-1} and r_{12}^{-2} for singlet and triplet states.

State designations		Singlet matrix elements		Triplet matrix elements	
α	β	$\langle\psi_\alpha^{(S)}\vert r_{12}^{-1}\vert\psi_\beta^{(S)}\rangle$	$\langle\psi_\alpha^{(S)}\vert r_{12}^{-2}\vert\psi_\beta^{(S)}\rangle$	$\langle\psi_\alpha^{(T)}\vert r_{12}^{-1}\vert\psi_\beta^{(T)}\rangle$	$\langle\psi_\alpha^{(T)}\vert r_{12}^{-2}\vert\psi_\beta^{(T)}\rangle$
1	1	0.191 406 24	0.058 333 33	0.132 812 50	0.022 619 05
2	2	0.092 843 32	0.014 611 57	0.087 181 00	0.010 537 10
3	3	0.089 896 65	0.015 378 68	0.083 615 03	0.009 544 11
4	4	0.054 971 77	0.006 051 81	0.053 014 82	0.004 562 89
5	5	0.053 481 90	0.006 413 35	0.051 320 90	0.004 243 50
6	6	0.121 852 75	0.028 001 14	0.105 658 54	0.014 579 37
7	7	0.065 573 67	0.010 998 96	0.060 181 21	0.005 829 59
8	8	0.041 302 99	0.005 473 63	0.038 793 12	0.002 935 02
1	2	0.020 583 72	0.011 697 87	0.021 244 92	0.006 847 62
1	3	0.033 529 33	0.018 439 53	0.019 514 70	0.006 289 94
1	4	0.008 503 54	0.005 362 56	0.011 111 01	0.003 903 27
1	5	0.017 199 19	0.010 291 07	0.009 937 99	0.003 491 19
1	6	0.039 073 94	0.023 891 68	0.013 239 26	0.003 636 44
1	7	0.022 712 20	0.015 103 57	0.007 624 78	0.002 272 06
1	8	0.015 365 16	0.010 567 14	0.005 163 07	0.001 588 58
2	3	0.019 757 20	0.008 702 30	−0.003 720 28	0.000 485 51
2	4	0.022 158 19	0.006 719 25	0.018 991 02	0.004 355 53
2	5	0.009 397 34	0.005 149 58	−0.000 160 03	0.000 476 39
2	6	−0.011 462 17	−0.000 586 54	−0.011 152 03	−0.002 266 86
2	7	0.002 798 20	0.001 919 99	0.001 869 45	0.000 111 46
2	8	0.003 131 47	0.001 823 93	0.002 184 96	0.000 336 71
3	4	0.007 103 90	0.004 314 19	0.001 396 76	0.000 777 75
3	5	0.022 509 83	0.007 590 14	0.018 879 49	0.004 070 45
3	6	0.004 387 50	0.005 702 07	0.005 266 75	0.001 908 11
3	7	0.005 616 41	0.004 741 10	0.001 271 38	0.000 732 12
3	8	0.004 373 17	0.003 594 70	0.000 649 70	0.000 432 07
4	5	0.007 750 32	0.003 136 28	−0.002 701 25	0.000 069 32
4	6	−0.005 220 29	−0.001 016 13	−0.004 053 89	−0.001 141 60
4	7	−0.005 076 30	−0.000 182 27	−0.004 982 63	−0.000 698 17
4	8	−0.000 355 09	0.000 332 71	−0.000 471 41	−0.000 164 96
5	6	0.002 053 28	0.002 924 72	0.002 584 56	0.001 072 91
5	7	0.001 841 97	0.002 385 23	0.001 627 76	0.000 583 12
5	8	0.001 923 83	0.001 887 43	0.000 652 97	0.000 325 45
6	7	0.031 968 82	0.013 817 99	0.022 867 08	0.005 650 13
6	8	0.018 415 11	0.009 023 14	0.012 362 40	0.003 408 93
7	8	0.020 831 69	0.006 715 58	0.017 168 77	0.003 105 06

tribute much more strongly to $\sigma(\mathcal{E}_T)$ than they do to $\mathcal{E}_T$ itself, because the calculation of σ involves the square of the energy difference $(\mathcal{E}_T - e_i)^2$ whereas $\mathcal{E}_T$ involves only the first power of $\mathcal{E}_T - e_i$, e_i being the energy of the ith configuration. Thus it is seen why the variational upper bound to the energy is so good whereas the σ-dependent lower bound is so poor. At present, investigations to calculate σ for alternative basis sets (e.g., the Hylleraas set of Bhatia, Temkin, and Perkins) which should incorporate improved interelectron correlation are under way.

It should be pointed out that, notwithstanding the fact that the lower bounds with this basis set are poor, these results nonetheless establish lower bounds which bracket two as yet unobserved levels.

V. ACKNOWLEDGMENTS

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TABLE III. Coefficients of the first-three $^1P^o$ and $^3P^o$ states in helium and the values of σ for these configurations. This table gives the coefficients a_α as required in Eq. (1) for the lowest three odd parity singlet P auto-ionizing states (which are labeled S_1, S_2, S_3) and the lowest three odd parity triplet P auto-ionizing states (which are labeled T_1, T_2, T_3). These coefficients were taken from Lipsky and Russek.[3] It must be noted, however, that the basis states used here are the hydrogenic product configurations, and not the Cooper, Fano, and Prats[10] combination used in Lipsky and Russek. Also given in this table are the values of σ for these six states, where σ is defined by $\sigma = \langle\phi\,|(H-E)^2|\,\phi\rangle = \langle\phi|H^2|\phi\rangle - \langle\phi|H|\phi\rangle^2$, $E = \langle\phi|H|\phi\rangle$.

Product hydrogenic configuration	Coefficient of each configuration Singlet states S_1	S_2	S_3	Triplet states T_1	T_2	T_3
$2s\,2p$	0.877 39	−0.008 46	−0.190 14	0.955 72	0.168 87	−0.026 96
$2s\,3p$	−0.186 73	0.647 88	−0.338 97	−0.194 79	0.529 67	−0.488 65
$3s\,2p$	−0.304 51	−0.626 63	−0.420 33	−0.173 82	0.564 71	0.590 56
$2s\,4p$	−0.027 72	−0.257 10	0.386 86	−0.056 06	−0.403 73	0.247 50
$4s\,2p$	−0.056 52	0.235 96	0.585 05	−0.047 99	−0.400 91	−0.330 48
$2p\,3d$	−0.301 44	0.219 42	−0.151 49	−0.106 48	0.130 08	−0.393 16
$2p\,4d$	−0.074 21	−0.129 71	0.395 97	−0.033 30	−0.175 55	0.292 84
$2p\,5d$	−0.047 28	−0.027 29	−0.023 57	−0.023 26	−0.023 35	0.029 98
σ (in a.u.^{2})	0.014 84	0.000 61	0.002 75	0.007 36	0.003 37	0.000 70
$\sigma^{1/2}$ (in eV)	3.318	0.672	1.428	2.334	1.578	0.721

VI. APPENDIX

It will now be shown that the eigenspectrum of Q_1HQ_1 has the same "window" in the continuous part of the spectrum [Eq. (49c)] as does R_1HR_1. Reference to Fig. 4 will make the derivation easier to follow. We assume that H has no true discrete stationary states embedded in the continuum (i.e., that any levels experimentally observed in the continuum of H are quasistationary, or auto-ionizing states). Thus the eigenspectrum of H consists of a set of discrete levels below the first ionization energy. Above this is the continuum spectrum which, in some energy regions, is multiply degenerate. On the other hand, the eigenspectrum of Q_THQ_T consists, by hypothesis, of a single point $\mathcal{E}_T$, while the eigenspectrum of $(1-Q_T)H(1-Q_T)$ will be in a one-to-one correspondence with the eigenspectrum of H. This can be established by a simple extension of the arguments presented below, but is not pertinent to our development. All that is required is that $(1-Q_T)H(1-Q_T)$ possesses a continuum spectrum degenerate with $\mathcal{E}_T$. And this must, of course, be true if the state ϕ_T decays to an ionized state. As mentioned before, those states in the continuum spectrum in the energy region

$$\mathcal{E}_T - \delta E \leqslant \epsilon \leqslant \mathcal{E}_T + \delta E$$

are placed in P_1 space by definition. They are eigenfunctions of P_1HP_1 as well. To establish this we write

$$(1-Q_T)H(1-Q_T) = (P_1+R_1)H(P_1+R_1). \quad (54)$$

Letting v_ϵ be any eigenstate of (54) placed in P_1 space, we have

$$(P_1+R_1)H(P_1+R_1)v_\epsilon = \epsilon v_\epsilon\ . \quad (55)$$

Since $R_1v_\epsilon = 0$, we have

$$(P_1+R_1)HP_1v_\epsilon = \epsilon v_\epsilon\ . \quad (56)$$

Finally, multiplication of both sides of (53) by P_1 yields

$$P_1HP_1v_\epsilon = \epsilon v_\epsilon\ , \quad (57)$$

which is the desired result.

It now remains to establish that the eigenspectrum of Q_1HQ_1, where $Q_1 = Q_T + R_1$, has one and only one level in the energy interval

$$\mathcal{E}_T - \delta E \leqslant E_1 \leqslant \mathcal{E}_T + \delta E\,.$$

Theorem II immediately proves that there is one level in this energy range, since it holds that any extension of Q_T space must have a level in this range. Finally, it must be shown that configuration interaction between any v_ϵ placed in R_1 space with ϕ_T will not perturb ϵ to move it into the energy range included in P_1 space. In fact we will prove more than that. We will show that the continuum spectrum of Q_1HQ_1 is identical with that of R_1HR_1.

To this end we consider a continuum eigenfunction of Q_1HQ_1 belonging to eigenvalue ϵ:

$$Q_1HQ_1w = \epsilon w\ . \quad (58)$$

Now w can be represented as a linear combination of some element v in R_1 space plus ϕ_T:

$$w = v + a\phi_T\,, \quad R_1 v = v,$$

$$Q_T\phi_T = \phi_T\,, \quad Q_T v = R_1\phi_T = 0\,. \tag{59}$$

Substituting (59) into (58) we obtain

$$Q_1HQ_1w = (Q_T + R_1)H(Q_T + R_1)(v + a\phi_T)$$
$$= \epsilon(v + a\phi_T)\,. \tag{60}$$

Multiplying first by Q_T and then by R_1 and using the property that $Q_TR_1 = 0$, Eq. (60) is decomposed into two coupled equations:

$$aQ_THQ_T\phi_T + Q_THR_1v = \epsilon a\phi_T\,, \tag{61a}$$

$$aR_1HQ_T\phi_T + R_1HR_1v = \epsilon v\,. \tag{61b}$$

Since w has infinite norm, by hypothesis, while ϕ_T is a normalized function, it follows that v must also have infinite norm. Moreover, as either r_1 or r_2 approaches infinity, the first term on the left-hand side of Eq. (61b) must vanish asymptotically. This is so because ϕ_T, and hence $H\phi_T$, have finite norm. The projection operator R_1 which postmultiplies this term can only decrease the norm. Consequently, $R_1HQ_T\phi_T$ has finite norm and must therefore vanish as $O(r_1^{-2}r_2^{-2})$. It therefore follows that asymptotically

$$R_1HR_1v = \epsilon v, \quad \text{as} \quad r_1 \text{ or } r_2 \to \infty\,. \tag{62}$$

Equation (62) is not an eigenvalue equation; it is only an asymptotic relationship. However, writing down an eigenvalue equation for a continuum eigenfunction of R_1HR_1,

$$R_1HR_1(v + u) = \epsilon'(v + u)\,, \tag{63}$$

and requiring that the asymptotic limit of (63) reduces to (62), yields

$$\epsilon' = \epsilon\,, \tag{64}$$

and that u and R_1HR_1u each vanish asymptotically as $O(r_1^{-2}r_2^{-2})$. In other words, u is just a normalizable packet constructed from elements of R_1 space. Thus it has been shown that any continuum eigenvalue of R_1HR_1 is also a continuum eigenvalue of Q_1HQ_1. Clearly, this same argument can be used to demonstrate that any continuum eigenvalue of $(1 - Q_T)H(1 - Q_T)$ must also be a continuum eigenvalue of H by simply replacing Q_1 in the above argument by unity.

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[1] H. Feshbach, Ann. Phys. (N. Y.) 5, 357 (1958); 19, 282 (1962).

[2] T. F. O'Malley and S. Geltman, Phys. Rev. 137, A1344 (1965).

[3] L. Lipsky and A. Russek, Phys. Rev. 142, 59 (1966).

[4] P. L. Altick and E. N. Moore, Phys. Rev. Letters 15, 100 (1965).

[5] Y. Hahn, T. F. O'Malley, and L. Spruch, Phys. Rev. 134, B911, B396, (1964).

[6] A. K. Bhatia, A. Temkin, and J. F. Perkins, Phys. Rev. 153, 177 (1967).

[7] A. F. Stevenson and M. F. Crawford, Phys. Rev. 54, 375 (1938).

[8] See, e.g., L. I. Schiff, Quantum Mechanics (McGraw-Hill Book Company, Inc., New York, 1955), 2nd ed., Sec. 29. With the normalization used here, the density of final states is equal to unity.

[9] P. G. Burke and D. D. McVicar, Proc. Phys. Soc. (London) 86, 989 (1965).

[10] J. W. Cooper, U. Fano, and F. Prats, Phys. Rev. Letters 10, 518 (1963).