Inelastic-resonance quasiprojection operators

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An explicit form of quasiprojection operator $\hat{Q}$ is given for the calculation of resonances in the domain of inelastic scattering of electrons from atoms and atomic ions. This operator allows the calculation of the resonant spectrum through the diagonalization of $\hat{Q}H\hat{Q}$ with as many inelastic states projected out as desired. The technique gives rise to a limited number of spurious states, but they can be unambiguously identified and thus eliminated. The elimination procedure is illustrated in the case of three-electron (i.e., heliumlike target) ions whereby we explicitly determine the number of spurious states that arise in inelastic scattering below the $3\,^3S$ state of the target.

I. INTRODUCTION

Although recent work in the theory and calculation of resonant structures in the scattering of electrons from atoms was started as a purely academic exercise, which can be described as the culmination of the nuclear-resonance theory in the area of atomic physics, it has very recently become clear that such calculations on ionized systems are of essential practical importance in solar, plasma, and astrophysics. For the scattering cross sections in the neighborhood of inelastic thresholds can be dominated by these resonances,[1] and as a result, the associated rate constants can be dominated by such effects. The rate constants are in turn the dominant atomic parameters which are required in order to interpret the physical conditions of the astrophysical or other plasma.

As a matter of practice resonance calculations can only be described as rigorous for one-electron targets, because ultimately only in that case can the exact (i.e., hydrogenic) target function be explicitly given.

The underlying method we wish to consider is the resonant projection-operator technique of Feshbach.[2] Here the restriction to electron scattering from one-electron targets manifests itself by the fact that only in that case can a rigorous projection operator Q be constructed.[3] This then allows bounded variational calculations for QHQ to be carried out[4] whose eigenspectrum corresponds faithfully to resonances of the compound system. Such calculations have in the interim been greatly refined, so that considerable precision has now been obtained.[5]

In calculating many-electron targets, one would naturally be led to use the expedient of approximate target-state wave functions in an otherwise rigorous form of Q. It turns out, however, because of identity of scattered and orbital electrons, that even the formal definition of an idempotent Q operator[2] is not explicit; rather Q contains a part that requires the solution of a subsidiary homogeneous integral equation which would in general pose a very formidable problem. To obviate this problem, we have observed,[6] in effect, that dropping this very difficult piece of the operator affects neither the discreteness of the spectrum nor the proximity of eigenvalues to the positions of resonances. At the same time all the effects of the antisymmetry of the total wave function are retained in this quasi-projection-operator formalism. The original calculations for both position and width of the lowest ^2S states of He$^-$ have provided results[6] which are among the most accurate thus far. Similar successful calculations for positions and widths of Li autoionization states have also been carried out.[7]

The method[6] actually consists of replacing the Q operator by a (generally nonidempotent) $\hat{Q}$ operator from which the variational solution of $\hat{Q}H\hat{Q}$ proceeds in the usual way. However the previous $\hat{Q}$ and associated calculations were restricted to resonances below the first inelastic threshold.[6] In this paper we generalize the operators to be applicable to resonances below any number of target excited states, but below the first ionization threshold (Sec. II).

The analysis shows that as in the previous case,[6] one can get spurious states, which, however, can unambiguously be determined (and probably in advance). Although the general nature of these states is clear, the specific analysis is performed for the two-electron target, with the results being displayed in a table giving the number of spurious states of different total angular momenta (partial waves) for quasi-projection-operators which successively exclude up to five states (i.e., all states below the $3\,^3S$ state of the target). This appears in Sec. III.

In Sec. IV, we present our conclusions, which include some comments and contrasts with other ap-

proaches to the inelastic resonance problem. We also discuss the incorporation of these ideas in a distorted-wave program devoted to solar and astrophysical problems.

II. INELASTIC RESONANCE QUASI-PROJECTION-OPERATORS

The basic operator we define is the $\hat{P}$ operator

$$\hat{P}_\nu = \sum_{n=0}^{\nu} \sum_{i=1}^{N+1} P_i^{(n)} . \tag{2.1}$$

$\hat{P}_\nu$ is such that it does not affect the asymptotic form of a scattering wave function Ψ when $\nu + 1$ channels are open:

$$\lim_{r_j \to \infty} \hat{P}_\nu \Psi = \lim_{r_j \to \infty} \Psi \tag{2.2}$$

In the electron-atom (-ion) problem this must be true for the radial coordinate of every electron r_i, $i = 1, 2, \ldots, N+1$, where N is the number electrons in the target (so that $N+1$ is the total number of electrons). The $\hat{Q}$ operator is then defined by

$$\hat{Q}_\nu = 1 - \hat{P}_\nu ; \tag{2.3}$$

it follows from (2.2) that

$$\lim_{r_j \to \infty} \hat{Q}_\nu \Psi = 0, \quad i = 1, 2, \ldots, N+1 . \tag{2.4}$$

The index n in (2.1) labels the target states and ν the highest state which is energetically accessible for a given incident energy k_0^2. (Rydberg units are used throughout this paper.) Letting E be total energy,

$$E = k_0^2 + \epsilon_0 = k_1^2 + \epsilon_1 = \ldots = k_n^2 + \epsilon_n, \quad n \leq \nu , \tag{2.5a}$$

whereas

$$E < \epsilon_{\nu+1} . \tag{2.5b}$$

In (2.5) ϵ_n are the energies of the target system and k_n^2 the corresponding scattering energies

$$k_n^2 = k_0^2 - (\epsilon_n - \epsilon_0) . \tag{2.5c}$$

The projectors $P_i^{(n)}$ in (2.1) are defined by

$$P_i^{(n)} = \psi_n(r^{(i)}) \rangle \langle \psi_n(r^{(i)}), \tag{2.6}$$

where ψ_n is target wave function of the nth state coupled to the angles and spin of the scattered electron to make a function of good total orbital angular momentum (L) and total spin (S):

$$\psi_n(r^{(i)}) = \sum (L_n l_i M_L m_i | L\overline{M}_L)(S_n \tfrac{1}{2} M_S m_s | S\overline{M}_S)$$

$$\times \phi_n(x^{(i)}) Y_{l_i m_i}(\Omega_i) \chi_{m_s/2}(i) \tag{2.7}$$

In (2.7) we have specified explicitly the quantum numbers $n = (L_n, M_L, S_n, M_S)$ associated with the target eigenfunction ϕ_n only in the Clebsch-Gordan coefficients. In addition we use superscript notation to indicate the *absence* of a coordinate; thus in (2.7) $x^{(i)}$ signifies the *absence* of the totality of coordinates (spin and space) associated with the ith particle. Explicitly

$$\phi_n(x^{(i)}) = \phi_{L_n M_L, S_n M_S}(x_1, x_2, \ldots, x_{i-1}, x_{i+1}, \ldots, x_{N+1}).$$

We also note that the "argument" of ψ_n on the left-hand side of (2.7) is similarly consistent, because from the right-hand side ψ_n lacks only the radial coordinate r_i of the ith electron. $\chi_{m_s/2}(i)$ is a spin-$\frac{1}{2}$ function of the ith electron.

Before proving the fundamental relation, Eq. (2.2), we must specify the asymptotic form of a scattering wave function in the $n \leq \nu$ continuum. In the representation in which actual calculations are carried out (i.e., L and S are good quantum numbers)

$$\lim_{r_j \to \infty} \Psi = (-1)^{p_j} \sum_{n=0}^{\nu} \frac{\sin(k_n r_j + \sigma_n)}{k_n r_j} \psi_n(r^{(j)}) . \tag{2.8}$$

The factor $(-1)^{p_j}$ is ± 1 (i.e., $p_j = 0$ or 1) depending on whether the argument in (2.8) $(x_j, x_1, \ldots, x_{j-1}, x_{j+1}, \ldots, x_{N+1})$, is an *even* or *odd* permutation of $x_1, x_2, \ldots, x_{N+1}$. This is the necessary condition that the asymptotic form derives from a fully antisymmetric Ψ. It is assumed that the target states ϕ_n are themselves antisymmetric in their particle indices. The phase σ_n in (2.8) is the usual partial-wave term $-\frac{1}{2}\pi l_i$ plus the well-known Coulomb terms if the target is an ion.

We are now in position to prove the fundamental formula (2.2). Because the ϕ_n are bounded eigenfunctions we know

$$\lim_{r_j \to \infty} \phi_n(x^{(i)}) = 0, \quad i \neq j . \tag{2.9a}$$

If $i = j$, then ϕ_n does not contain r_j (i.e., it does not contain x_j) and it is unaffected by the limit; thus we can write more generally

$$\lim_{r_j \to \infty} \phi_n(x^{(i)}) = \phi_n(x^{(i)}) \delta_{ij} . \tag{2.9b}$$

We also use the orthonormality of the ϕ_n:

$$\langle \phi_n(x^{(j)}) \phi_{n'}(x^{(j)}) \rangle = \delta_{nn'} . \tag{2.10}$$

It follows then from (2.8) that

$$\lim_{r_j \to \infty} P_i^{(n)} \Psi = \delta_{ij} P_i^{(n)} \left(\lim_{r_j \to \infty} \Psi \right) . \tag{2.11}$$

With these equations we then outline below the essential steps by which Eq. (2.2) is derived:

$$\lim_{r_j \to \infty} \hat{P}_\nu \Psi = \sum_{n=0}^{\nu} \sum_{i=1}^{N+1} \lim_{r_j \to \infty} (P_i^{(n)} \Psi)$$

$$= \sum_{n=0}^{\nu} \sum_{i=1}^{N+1} \delta_{ij} P_i^{(n)} \left(\lim_{r_j \to \infty} \Psi \right)$$

$$= \sum_{n=0}^{\nu} (-1)^{p_j} \psi_n(r^{(j)}) \sum_{n'=0}^{\nu} \langle \psi_n(r^{(j)}) \psi_{n'}(r^{(j)}) \rangle$$

$$\times \frac{\sin(k_{n'} r_j + \sigma_{n'})}{k_{n'} r_j}$$

$$= \sum_{n=0}^{\nu} (-1)^{p_j} \frac{\sin(k_n r_j + \sigma_n)}{k_n r_j} \psi_n(r^{(j)})$$

$$= \lim_{r_j \to \infty} \Psi . \qquad (2.2)$$

To repeat: Eq. (2.2) is the essential property, because, as noted in (2.4) it follows that $\hat{Q}_\nu \Psi \to 0$ as any $r_j \to \infty$, and from that we have our desired variational principle:

$$\delta \left(\frac{\langle \Psi \hat{Q}_\nu H \hat{Q}_\nu \Psi \rangle}{\langle \hat{Q}_\nu \Psi, \hat{Q}_\nu \Psi \rangle} \right) = 0 \qquad (2.12)$$

whose eigenvalues $\mathcal{E}_\mu^{(\nu)}$ are *discrete* if they are below $\epsilon_{\nu+1}$.[6]

The denominator of (2.12) is

$$\langle \hat{Q}_\nu \Psi, \hat{Q}_\nu \Psi \rangle = \langle \Psi \hat{Q}_\nu^2 \Psi \rangle ; \qquad (2.13)$$

it is to be emphasized that (2.13) is not in general equal to $\langle \Psi \hat{Q}_\nu \Psi \rangle$, because the quasi-projection-operator $\hat{Q}_\nu$ is not in general idempotent. The lack of idempotency is in turn related to the (possible) appearance of a finite number of spurious eigenvalues. These will be discussed in Sec. III; however we emphasize that such eigenvalues can be identified unambiguously, and it is this fact that makes this method a secure one for calculating autoionization states.

III. SPURIOUS STATES

Let us envisage an arbitrary function Ψ (of good L and S) to be used in the variational calculation (2.12). Such a function can be expanded in the form

$$\Psi = \mathcal{A} \left(\sum_{n, m} C_{nm} \psi_n(r^{(j)}) \theta_m(r_j) \right) . \qquad (3.1)$$

The antisymmetrizer $\mathcal{A}$ effectively sums over cyclical permutations of the j index, i.e.,

$$\mathcal{A}[\psi_n(r^{(j)}) \theta_m(r_j)] = \sum_{j=1}^{N+1} (-1)^{p_j} \psi_n(r^{(j)}) \theta_m(r_j). \qquad (3.2)$$

Asymptotically the Q_ν operator gets rid of all target components ψ_n for $n \leq \nu$ according to (2.4). Now the key to the Feshbach Q-operator formalism[1] is that in order to get only eigenvalues which corres-

pond to resonances, the Q_ν operator should eliminate all $n \leq \nu$ components for *all* distances of the radial coordinate r_j. In (3.2) the r_j dependence of Ψ is expressed in terms of a complete set of radial orbitals $\theta_m(r_j)$. If the θ_m *were* orthogonal to the ψ_n for all $n \leq \nu$,

$$\langle \theta_m(r_j) \psi_n(r^{(k)}) \rangle_{j \neq k} = 0, n \leq \nu, \text{ all m} \qquad (3.3)$$

then it is easy to show that

$$\langle \Psi_1 \Psi_2 \rangle = (N+1) \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} C_{nm}^{(1)*} C_{nm}^{(2)}, \qquad (3.4)$$

whereas

$$\langle \Psi_1 \hat{P}_\nu \Psi_2 \rangle = (N+1) \sum_{n=0}^{\nu} \sum_{m=0}^{\infty} C_{nm}^{(1)*} C_{nm}^{(2)} . \qquad (3.5)$$

It is clear therefore that an arbitrary matrix element of $Q_\nu = 1 - P_\nu$ would be [if (3.3) were valid]

$$\langle \Psi_1 Q_\nu \Psi_2 \rangle = (N+1) \sum_{n=\nu+1}^{\infty} \sum_{m=0}^{\infty} C_{nm}^{(1)*} C_{nm}^{(2)}, \qquad (3.6)$$

from which we see that only $n \geq \nu+1$ terms remain.

In point of fact the orthogonality condition (3.3) is not in general true. Actually there will be a *finite* number of terms for which (3.3) will be violated. The number of such terms is in effect the number of spurious states that can arise. Below we shall consider explicitly the number of such terms for the two-electron target, but in a general way we can describe those orbitals which violate (3.3) as arising from orbitals which (in an independent-particle approximation) correspond to unfilled shells in the ϕ_n. For example if we want to eliminate both the ground, $1\,^1S(1s^2)$, and first excited, $2\,^3S(1s2s)$, states from a two-electron target, then a three-electron wave function of the form $(1s)^2\,^1S; (2s)|\,^2S\rangle$, $(1s2s)\,^3S; (1s)|\,^2S\rangle$, and $(1s2s)\,^3S; (2s)|\,^2S\rangle$ all contain the third electron in an orbital occupied by one of the target electrons. None of those types of functions will be completely eliminated by the appropriate $\hat{Q}$ operator (in this case $\hat{Q}_2$). On the other hand a hypothetical state in which a target-state orbital would appear to be occupied such as $(1s)^2\,^1S; (1s)|\,^2S\rangle$ is disallowed, as is well known, by the exclusion principle. Such a hypothetical state therefore does not contribute a spurious state.

In Table I we have tabulated the number of spurious states which will arise for different ν up to $\nu = 4$. This number is derived by writing all allowable combinations $\Psi_n\rangle$ (for each total symmetry) of target orbitals which can be made from those of occupied target orbitals, and then calculating $Q_\nu \Psi_n\rangle$; the number of nonzero $Q_\nu \Psi_n\rangle$ consititues the

TABLE I. Number of spurious states in quasiprojection calculation for three-electron ions.

Symmetry of autoioziation state[b]	$\nu+1$ target state[a]	1 $2\,^3S\,(1s\,2s)$	2 $2\,^1S\,(1s\,2s)$	3 $2\,^3P\,(4s\,2p)$	4 $2\,^1P\,(1s\,2p)$	5 $3\,^3S\,(1s\,3s)$
$^2S^e$		0	2	2	3	3
$^2P^o$		0	0	0	4	5
$^2D^e$		0	0	0	1	1

[a] The target state given is the one *below* which eigenvalues must lies in order to be considered as resonances. See text for further discussion.

[b] There are no spurious states of higher symmetry for $\nu \leqslant 5$. States which are nonrelativistically stable are not included in this table.

number of spurious states, and it is the entry in Table I. In so doing care must be exercised that (a) the state is allowable, (b) that each state is linearly independent of the others, and (c) that even if some states are linearly independent the resultant $\hat{Q}_\nu\Psi$ must also be linearly independent, but not zero. In the determination of these numbers it is only necessary to use Slater determinantal forms for the target-state functions. Furthermore one does not use the numerical values of the orbitals, only the fact that they are orthonormal:

$$\langle (nl),\ (n'l')\rangle = \delta_{nn'}\delta_{ll'}\ . \tag{3.7}$$

We have illustrated (a) above by noting that $(1s)^2\,^1S,(1s)\,|\,^2S\rangle$ does not exist; to illustrate (b) we note that

$$\Psi_n = (1s2s)\,^1S;\ (1s)\,|\,^2S\rangle \propto (1s)^2\,^1S;\ (2s)\,|\,^2S\rangle\ .$$

$$\propto (1s2s)\,^3S;\ (1s)\,|\,^2S\rangle\ .$$

Thus these somewhat different looking states are to be counted only once. We also note that in $^2P^o$ symmetry the three states $(1s)^2\,^1S;\ (2p)\,|\,^2P\rangle$, $(1s2s)\,^3S;\ (2p)\,|\,^2P\rangle$, and $(1s2s)\,^1S;\ (2p)\,|\,^2P\rangle$ are zero when acted on by $\hat{Q}_0$, $\hat{Q}_1$, and $\hat{Q}_2$; thus they contribute no spurious states. On the other hand for $\nu=3$ these states plus the remaining possibilities $(1s2p)\,^3P;\ (1s)\,|\,^2P\rangle$ and $(1s2p)\,^3P;\ (2s)\,|\,^2P\rangle$ are *not* zero when acted on by $\hat{Q}_3$; however two of the resultant $\hat{Q}_3\Psi_n$ are proportional to each other, so that only four spurious states remain, as indicated in Table, I, for this case.

Let us also emphasize that, discounting the spurious states, the energy of the autoionization state must be below $\epsilon_{\nu+1}$ in order for it to count:

$$\mathscr{E}^{(\nu)} < \epsilon_{\nu+1}\ . \tag{3.8}$$

(The $\nu+1$ state is what is given in the table.) However any state which does qualify is distinctly a new state (i.e., resonance), and not one which may have arisen from a lower (or higher) ν calculation. In fact the spurious states of a given ν calculation

may in fact correspond to the real resonance of a lower ν calculation. (The spurious states, however, may also correspond to a purely nonresonant scattering function.) Thus we envisage calculations as being performed sequentially from one ν to the next, so that one uncovers all (Feshbach) resonances that are present.

We expect that the energy of spurious states will always be the lowest that arise. Thus, for example, for the $\nu+1 = 3$, $^2S^e$ entry in Table I, we expect the lowest two eigenvalues to correspond to the spurious states, and, assuming we have used a good enough variational wave function these eigenvalues should be below the $2\,^3P$ threshold. However, in order to be sure, it may be necessary to evaluate $\langle\Psi_n\Psi\rangle$ for each eigenfunction Ψ that arises for each suspected spurious configuration Ψ_n. If this overlap is in fact large (i.e., close to 1), then we can be sure that the (main part of the) variational eigenfunction Ψ is Ψ_n in character and should be eliminated. It is conceivable that in some cases a nonobvious ordering of eigenfunctions may occur; but in any case the overlap test will clearly reveal which states are real.

Finally we mention that no attempt has been made to include the shift Δ between the eigenvalues $\mathscr{E} = \langle QHQ\rangle$ and true resonance position[2] E_r:

$$E_r = \mathscr{E} + \Delta\ .$$

Indeed it makes no sense to do so in the absence of exact target states and idempotent Q and P operators. From the case of one-electron targets, where Δ can be calculated,[5] one can be sure that Δ will be very small, probably much smaller than other uncertainties which will necessarily confront any real calculation.

IV. CONCLUSION

In generalizing the quasi-projection-operator technique to the inelastic domain, we have attempted to develop a method which is well defined, interpretatively unambiguous, and accurate. The need for accuracy in terms of solar, astrophys-

ical as well as plasma spectral diagnostics was mentioned in the Introduction. A preliminary investigation by Pindzola, Temkin and Bhatia[8] for resonances from O VII suggests that resonances are not important there. However the conclusion depends heavily on the widths; since that calculation[8] is an effective separable approximation for the doubly excited states (further using a distorted-wave, multichannel quantum-defect formalism[9]), it is not at all clear what the accuracy of those calculated resonances is. With the implementation of the present quasi-projection-operator technique we can confidently look forward to a significant increase in accuracy.

There is a more subtle need for the quasi-projection-operator formalism which arises in the calculation of highly ionized systems. As the charge of the nucleus increases relative to (a fixed) number of orbital electrons, it is known that the position of autoionization states descend, relative to target threshold. In fact they can cross target thresholds,[10] and in the case of highly charged ions they can surely cross several thresholds. This means that autoionization states in a given region may be related to parent (target) states of much higher principal quantum number. However in close-coupling or related calculations each target state is included explicitly, so that one is in practice restricted to including only a few of such states. On the other hand, in a quasi-projection-calculation the resonant function $\hat{Q}_\nu \Psi$ are not so restricted; one simply calculates the resonances

with (hopefully) as many parameters as is required for effective convergence. If in fact one cannot readily say from what parent state a given resonant state arises, it does not really matter. What does matter is that it is there, and it has a definite width.

A simple form of quasi-projection-operator calculation consists of an expansion in terms of orthonormal orbitals from which appropriate combinations are used to describe target states (up to νth) and one then constructs Ψ from products of the whole orthonormal set of orbitals such that Ψ is manifestly orthogonal to all ν target states. This is a generalization of the approach Weiss and Krauss[11] used to calculate He⁻ and Li autoionization states below the first excited threshold. Junker and one of the present authors (A.T.) are presently using this approach for He⁻, but we do not have any results to report at this time.

To conclude, we mention some other techniques which might be contemplated. The stabilization approach[12] contains much good physics; however, questions of interpretation are not as straightforward and they become more difficult for higher resonances and those above inelastic thresholds.

Complex-rotation methods[13] on the other hand have developed very rapidly and particularly the analytic aspects of this methodology have proved very rewarding mathematically.[14] Whether such methods will be amenable to the productive needs of many-electron systems[15] of interest in space and plasma physics remains to be seen.

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