Construction of resonance projection operators: Application to two-electron targets

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A derivation of resonance projection operators, in the Feshbach sense, is presented in detail, with inclusion of angular momentum and spin variables. The resultant operators, P and Q, are written in a transparent and manifestly symmetric form. The operators depend on eigensolutions of a homogeneous integral equation. The equation is solved and hence the operators are explicitly constructed for the two-electron (i.e., He-like) targets in a nonseparable (the open-shell) approximation; this procedure can readily be extended to any configuration-interaction-type target function. The kernel of the auxiliary integral equation is also explicitly derived for a Hylleraas-type target function; a Rayleigh-Ritz variational principle is written down for its eigenfunctions. It is pointed out that these (Feshbach) P and Q operators are *not* formally idempotent, but it is shown that their matrix elements between antisymmetric functions are. This makes them completely suitable for calculation of autoionization states via diagonalization of QHQ. A basic problem in using the concomitant optical potential for scattering calculations remains and is briefly discussed. The generalization of these operators to the inelastic domain is also given (in an appendix).

I. INTRODUCTION

It is by now well known that although the Feshbach projection-operator formalism was introduced in the context of nuclear physics,[1] its major quantitative applications have been in atomic physics. In point of fact even in the atomic context, the most rigorously quantitative applications have been confined to one-electron (i.e., H-like) targets, not only because the target eigenfunctions—in terms of which the projection operators are expressed—are known exactly, but also for the reason that the form of the operators which preserve antisymmetry can readily be inferred.[2] Historically, in fact, only subsequently was it shown[3] that those P and Q operators are equivalent to the prescription given by Feshbach[1] for the $N=1$ target.

That prescription for general N is the subject of this paper. For it is clear from a study of Ref. 1 that the Feshbach derivation was heuristically intended in the sense that angular momentum considerations are at best only implicit, and spin coordinates are not mentioned at all. Those defects can be remedied by defining a channel wave function in which the orbital and spin angular momenta are explicitly coupled to that of the incident electron.[4] From such functions one can construct a symmetry-preserving operator whose main additional component depends on a set of radial eigenfunctions $v_\alpha(r)$, which are the eigenfunctions of an integral equation, whose kernel is the heart of the method of construction.

In Sec. II we will completely define the elements of that derivation, but only briefly describe the derivation itself. The operators so derived are still somewhat symbolic in that the $v_\alpha(r)$ must somehow be solved for. This is done in Sec. III for an open-shell approximation of the He-like target. This same method can be used to derive explicit operators for any $N=2$ configuration-integration-type wave function whose coefficient functions are exponentials times powers of the two radial variables.

However, the most incisive wave functions for two-electron targets are of the Hylleraas-type. The kernel of the integral equation for v_α and its eigenvalue λ_α is explicitly derived in Sec. IV; as expected it is naturally expressed in terms of the variables $r_<, r_>$ in addition to r_1, r_2. Because of that, the $v_\alpha(r)$ and λ_α have not been analytically obtained; nevertheless, one can readily write down a (Rayleigh-Ritz) variational principle for them, and since the $v_\alpha(r)$ are functions of one radial variable, it is likely that such numerical or analytical variational solutions will be the most convenient for resonance calculations.

Section V is devoted to the question of idempotency, which in many respects is the most interesting question of the Feshbach formalism. For the basic requirement of Feshbach's theory is that it starts with the specification of the form of $P\Psi$, not P itself. Nevertheless, a form of an operator P is derived which necessarily has the property $P^2\Psi=P\Psi$. However, that does not answer the question of idempotency of P as an operator. That question is even more relevant for the operator $Q=1-P$, because in actual calculations Q operates on a function Φ which is antisymmetric but is otherwise arbitrary in form. What we will show is that the *operator* Q (and hence P) is *not* idempotent (for $N>1$ targets); i.e., $Q^2\neq Q$ as an operator identity; nevertheless, we shall also show that matrix elements $\langle \Phi_m Q^2 \Phi_n \rangle = \langle \Phi_m Q \Phi_n \rangle$ for arbitrary Φ_m and Φ_n providing the latter are completely (anti-) symmetric in spin and space.

The above are the paramount considerations regarding resonance (parameter) calculations. However, effective, idempotency is not the only essential feature required of the optical potential as far as general scattering calculations go. The paper concludes with a few remarks on that subject.

II. DERIVATION OF P AND Q

It is a basic item that Feshbach projection operators are expressed in terms of outer products involving ϕ_0, the (ground) state of the target system[1] (assumed here to be an atom or atomic ion with nucleus fixed). In order to include all coordinates explicitly, one introduces a channel wave function[4] in which the ground state is coupled to the angular momentum and spin of a partial wave of the incoming electron:

$$\psi_0(r^{(1)})=\sum(L_0 l_i M_0 m_i \mid LM)(S_0\tfrac{1}{2}M_{S0}m_s \mid SM_S) \times\phi_0(x^{(i)})Y_{l_i m_i}(\Omega_i)\chi_{1/2\,m_s}(i) . \tag{2.1}$$

[We are assuming LS (i.e., Russel-Saunders) coupling throughout.] It is emphasized that in contrast to Ref. 4, we are here only concerned with scattering from the ground state of the target system and, correspondingly, resonances in the purely elastic region. The generalization to the inelastic domain is given in Appendix B. In (2.1) aside from the obvious notation, $x^{(i)}$ indicates the *absence* of the ith electron coordinates from the total $(N+1)$-electron coordinates in the electron-target system. The x_i are the totality of the coordinates (spin and space) describing the ith electron, so that $x^{(i)}$ signifies

$$x^{(i)}=(x_{i+1},x_{i+2},\ldots,x_{N+1},x_1,\ldots,x_{i-1}) . \tag{2.2}$$

Equation (2.2) implies that the target has N electrons and by analogy $r^{(i)}$ in (2.1) indicates the absence of r_i:

$$r^{(i)}=(\Omega_i,s_i;x^{(i)}) . \tag{2.3}$$

Finally, we let p_i represent a cyclic permutation, so that

$$(-1)^{p_i}=\text{parity of}\begin{bmatrix}1 & 2 & \cdots & \cdots & \cdots & N+1\\ i & i+1 & \cdots & N+1 & \cdots & i-1\end{bmatrix} . \tag{2.4}$$

Note for $(N+1)$ odd, $(-1)^{p_i}=1$ for all i, whereas for $(N+1)$ even, $(-1)^{p_i}=(-1)^{i-1}$. For all N, $(-1)^{p_1}=1$.

With these notational preliminaries in hand, we start with the primary item of the Feshbach construction: the form of $P\Psi$, where Ψ is to be considered the exact, antisymmetric solution of the (many-electron) Schrödinger equation and, by definition

$$P\Psi\equiv\sum_{i=1}^{N+1}(-1)^{p_i}u(r_i)\psi_0(r^{(i)}) . \tag{2.5}$$

Here $u(r_i)$ are radial (scattering) orbitals which have not as yet been specified, but they must have the asymptotic property

$$\lim_{r_i\to\infty}u(r_i)=\frac{\sin(kr_i-\pi l_i/2+\sigma_i)}{kr_i} , \tag{2.6}$$

which guarantees that $P\Psi$ has the same asymptotic form as Ψ itself:

$$\lim_{r_i\to\infty}P\Psi=\lim_{r_i\to\infty}\Psi =(-1)^{p_i}\frac{\sin(kr_i-\pi l_i/2+\sigma_i)}{kr_i}\psi_0(r^{(i)}) . \tag{2.7}$$

Because $u(r_i)$ is defined for all values of r_i (eventually as the solution of the optical potential equation), Eq. (2.5) is more than a statement of the asymptotic property of $P\Psi$. We shall find that is an essential element of the construction in general; in fact *the basic condition is that the operator* Q,

$$Q=1-P, \tag{2.8}$$

be identically zero when projected on $\psi_0(r^{(i)})$ *for all values of* r_i:

$$\langle\psi_0(r^{(i)})Q\Psi\rangle_{r^{(i)}}=0 . \tag{2.9}$$

The identifying subscript in (2.9) indicates integration over $r^{(i)}$, which from (2.3) means integration over all coordinates except r_i. Again note that (2.9) is defined for all values of (any) r_i not just $r_i\to\infty$.

We shall obtain a specific form of Q by manipulating (2.9) to get an explicit (operator) expression operating on $\Psi\rangle$ (not $Q\Psi\rangle$) equal to zero. That operator will be Q. In doing that here, we will be very brief as the essential part of the derivation is given in Feshbach's paper[2] and we ourselves will give a detailed derivation elsewhere[5] as part of more general discussion of projection operators for many-electron systems.

The desired projection is defined as $w(r_i)$:

$$w(r_i)\equiv(-1)^{p_i}\langle\psi_0(r^{(i)})\Psi\rangle_{r^{(i)}} . \tag{2.10}$$

With the above, one can reexpress (2.9) in the form [using (2.8) and (2.5)]

$$w(r_i)=u(r_i)-\int_0^\infty K(r_i \mid r_j)u(r_j)r_j^2\,dr_j , \tag{2.11}$$

where the kernel K turns out to be

$$K(r_i \mid r_j)=(-1)^{p_i+p_j+1}N\langle\psi_0(r^{(i)})\psi_0(r^{(j)})\rangle_{r^{(ij)}} . \tag{2.12}$$

Here integration is over $r^{(ij)}$, which denotes all coordinates except r_i and r_j $(i\neq j)$.

The kernel K encapsulates exchange; its expansion in terms of v_α is a key aspect of the Feshbach approach.[1] The v_α (known as *natural orbitals* in quantum chemistry[6]) are the eigenfunctions of

$$v_\alpha(r_1)=\lambda_\alpha\int_0^\infty K(r_1 \mid r_2)v_\alpha(r_2)r_2^2\,dr_2 . \tag{2.13}$$

Specifically, from the eigensolutions of (2.13), which are discrete, orthonormal, and real,

$$\langle v_\alpha v_\beta\rangle\equiv\int_0^\infty v_\alpha(r)v_\beta(r)r^2\,dr=\delta_{\alpha\beta} , \tag{2.14}$$

one can expand K in the form

$$K(r_1 \mid r_2)=\sum_{\beta=1}^{n_\lambda}\frac{v_\beta(r_1)v_\beta(r_2)}{\lambda_\beta} . \tag{2.15}$$

This allows $u(r_i)$ to be related to $w(r_i)$: from (2.11)

$$u(r_i)=\sum_{\lambda_\alpha=1}v_\alpha(r_i)\langle v_\alpha u\rangle+w(r_i) +\sum_{\lambda_\beta(\neq1)}\frac{v_\beta(r_i)\langle v_\beta w\rangle}{\lambda_\beta-1} . \tag{2.16}$$

In this notation it is emphasized that v_β refers to the

eigenfunction associated with λ_β, not with β; thus v_α are associated with $\lambda_\alpha=1$ (if there are such eigenvalues); they are *not* simply the first eigenfunctions of the set. The eigenfunctions v_α make no contribution to the projection $\langle\psi_0 P\Psi\rangle$; one finds, rather, substituting the right-hand side (rhs) of (2.16) for $u(r_i)$ into $P\Psi$ of Eq. (2.5), that

$$\langle\psi_0(r^{(1)})P\Psi\rangle_{r^{(1)}}=\left\langle\psi_0(r^{(1)})\sum_{i=1}^{N+1}(-1)^{p_i}\left[w(r_i)+\sum_{\lambda_\beta}{}'\frac{v_\beta(r_i)\langle v_\beta w\rangle}{\lambda_\beta-1}\right]\psi_0(r^{(i)})\right\rangle_{r^{(1)}}. \tag{2.17}$$

The fact that $w(r_i)$ rather than $u(r_i)$ now appears on the rhs accomplishes our goal of allowing the left-hand side (lhs) of (2.17) to be expressed directly as a projection on $\Psi\rangle$, because using (2.10), one can then rearrange (2.17), inserting ket signs as appropriate, in its final form:

$$\langle\psi_0(r^{(1)})\,|\,P\Psi\rangle=\left\langle\psi_0(r^{(1)})\right|\sum_{i=1}^{N+1}\left[|\psi_0(r^{(i)})\rangle\langle\psi_0(r^{(i)})+\sum_{\lambda_\alpha}{}'\frac{v_\alpha(r_i)\psi_0(r^{(i)})\rangle\langle v_\alpha(r_i)\psi_0(r^{(i)})}{\lambda_\alpha-1}\right]|\Psi\rangle. \tag{2.18}$$

By comparison of the left- and right-hand sides of (2.18) one extracts the explicit form of P as an operator:

$$P=\sum_{i=1}^{N+1}\left[|\psi_0(r^{(i)})\rangle\langle\psi_0(r^{(i)})+\sum_{\lambda_\alpha}{}'\frac{v_\alpha(r_i)\psi_0(r^{(i)})\rangle\langle v_\alpha(r_i)\psi_0(r^{(i)})}{\lambda_\alpha-1}\right] \tag{2.19a}$$

with the Q operator given by (2.8), which we repeat here to emphasize that it too is rendered explicit through (2.19a):

$$Q=1-\sum_{i=1}^{N+1}\left[|\psi_0\rangle\langle\psi_0+\sum_{\lambda_\alpha}{}'\frac{v_\alpha\psi_0\rangle\langle v_\alpha\psi_0}{\lambda_\alpha-1}\right]. \tag{2.19b}$$

This is essentially equivalent to the operators derived by Feshbach.[1] In contrast to his forms, however, Eqs. (2.19) are manifestly symmetric in all $(N+1)$-particle coordinates, and by virtue of the definition of the channel function ψ_0, they contain the dependence on space and spin of all coordinates explicitly. For the eventual purposes of calculation, the v_α must be solved for, and in Sec. III we shall show that this can be done.

The generalization of these operators to ones applicable to resonances in the inelastic domain is given in Appendix B. It should be noted here that in all cases (elastic and inelastic) the parts of the respective operators which do *not* contain auxiliary functions (v_α) are just the quasiprojection operators we have previously introduced.[4]

III. AUXILIARY FUNCTIONS FOR THE $N=2$ ELECTRON TARGET

Before turning to the two-electron target, we reiterate that the projection operators independently written down for an $N=1$ (i.e., hydrogenic) target[2] were in fact subsequently derived from the Feshbach prescription by Hahn.[3] Again, more detail on this will be presented in our forthcoming review paper.[5]

We turn now to the $N=2$ target. First let it be emphasized that $N>1$ target eigenfunctions cannot be given analytically. Thus in one sense or another specific projection operators will always be non-exact, and they will depend on the approximation ϕ_0 of the target state. Let us start with the open-shell approximation of the ground state (^1S) in the form

$$\phi_0(x^{(3)})=\phi_0(x_1,x_2)=N_{\mu\nu}^{-1}[e^{-(\mu r_1+\nu r_2)}+(1\leftrightarrow 2)]\chi_0(1,2). \tag{3.1}$$

Note that ϕ_0 is a nonseparable function of r_1 and r_2; $N_{\mu\nu}^{-1}$ is a normalization constant and χ_0 is a spin singlet eigenfunction. By straightforward application of the formulas in Sec. II, using the fact that all cyclic permutations here are even,

$$(-1)^{p_1}=(-1)^{p_2}=(-1)^{p_3}=1, \tag{3.2}$$

one readily derives the channel functions

$$\psi_0(r^{(i)})=Y_{l0}(\Omega_i)\alpha_i\phi_0(x_j,x_k), \tag{3.3}$$

(i,j,k) corresponding to cyclic permutations of (1,2,3). In (3.3) α_i corresponds to spin up of the ith scattered electron (we could equally well have chosen it to be β_i—spin down).

The kernel is also easily found from (2.12) to be

$$K(r_1\,|\,r_2)=\frac{2(4\pi)^2}{N_{\mu\nu}^2}\delta_{l0}\left[\frac{e^{-\mu(r_1+r_2)}}{(2\nu)^3}+\frac{e^{(-\mu r_1+\nu r_2)}}{(\mu+\nu)^3}+(\mu\leftrightarrow\nu)\right]. \tag{3.4}$$

The Kronecker delta δ_{l0} emphasizes that in this approximation for ϕ_0, only for S states of the composite system will projection operators have components beyond the obvious $(\psi_0\rangle\langle\psi_0)$ ones. The normalization constant is explicitly given by

$$N_{\mu\nu}^2=(4\pi)^2[(2\mu\nu)^{-3}+8(\mu+\nu)^{-6}].$$

From (3.4) the auxiliary integral equation (2.13) is simply written down and solved. There are two solutions which

we here index by n [$n=1,2$ corresponds to $+$ and $-$ in (3.6)] in order to avoid confusion with spin α.

$$v_n(r)=C_{n1}e^{-\mu r}+C_{n2}e^{-\nu r} \tag{3.5}$$

with eigenvalues

$$\lambda_n^{-1}=\tfrac{1}{2}(1\pm 4\sqrt{K_{11}K_{22}}I_{12})\ , \tag{3.6}$$

where the K_{ij} are the coefficients of the various exponentials in (3.4) (note $K_{12}=K_{21}$), and I_{ij} are the integrals

$$I_{ij}\equiv\int_0^\infty e^{-(\gamma_i+\gamma_j)r}r^2\,dr=2/(\gamma_i+\gamma_j)^3 \tag{3.7}$$

with $\gamma_1=\mu$ and $\gamma_2=\nu$.

Finally, the eigenvector coefficients in (3.5) are related by

$$C_{n2}=C_{n1}\frac{(\lambda_n^{-1}-\frac{1}{2})}{2K_{12}I_{22}} \tag{3.8a}$$

with their absolute values determined from the normalization of each v_n, Eq. (2.15):

$$C_{n1}^2I_{11}+2C_{n1}C_{n2}I_{12}+C_{n2}^2I_{22}=1\ . \tag{3.8b}$$

This defines all elements of the P and Q operators:

$$P=\sum_{i=1}^{3}\left[|\psi_0(r^{(i)})\rangle\langle\psi_0(r^{(i)})| + \sum_{n=1}^{2}\frac{|v_n(r_i)\psi_0(r^{(i)})\rangle\langle v_n(r_i)\psi_0(r^{(i)})|}{\lambda_n-1}\right]. \tag{3.9}$$

As long as $\mu\neq\nu$ there is no $\lambda_n=1$ eigenvalue. (And for $\mu=\nu$ there is only one finite eigenvalue, for which $\lambda_n=1$, and the second sum drops out of P altogether.)

The same procedure can be extended to any configuration-interaction-type wave function

$$\phi_0(x_1,x_2)=\left[\sum_\lambda\varphi_\lambda(r_1,r_2)P_\lambda(\cos\theta_{12})\right]\chi_0(1,2)\ . \tag{3.10}$$

If φ_0 is expressed as exponential times powers

$$\varphi_0(r_1,r_2)\propto e^{-(\mu r_1+\nu r_2)}\sum_{m,n}C_{mn}r_1^mr_2^n+(1\leftrightarrow 2)\ , \tag{3.11}$$

then the eigenspectrum may similarly be analytically solved for. How far such a process would be worthwhile is not clear, for in the ground (^1S) state of He and its isoelectronic ions, the electrons have significant probability of getting close together and the target state wave function must have a cusp; that behavior can never be properly described by (3.10). The most natural ansatz which exhibits the necessary property is a Hylleraas-type expansion to which we now direct our attention.

IV. HYLLERAAS TARGET FUNCTIONS; A VARIATIONAL PRINCIPLE FOR THE AUXILIARY SPECTRUM

We write the spatial wave function for a Hylleraas-type expansion of the ground state (^1S) of the two-electron target:

$$\varphi_0(r_1,r_2,r_{12})=\frac{e^{-\gamma(r_1+r_2)}}{(8\pi^2)^{1/2}}\sum_{l,m,n}C_{lmn}(r_1^lr_2^m+r_1^mr_2^l)r_{12}^n\ . \tag{4.1}$$

Our aim is to derive the P operator for such an ansatz, and the first step is to evaluate the kernel K of the auxiliary integral eigenvalue equation (2.13):

$$K(r_1\,|\,r_2)=\frac{1}{4\pi}\int\varphi_0(r_2,r_3,r_{23})\varphi_0(r_3,r_1,r_{31})\,d\Omega_1\,d\Omega_2\,d^3r_3\ , \tag{4.2a}$$

which, inserting (4.1), can be written

$$K(r_1\,|\,r_2)=2e^{-\gamma(r_1+r_2)}\sum_{l,m,n}\sum_{l',m',n'}C_{lmn}C_{l'm'n'}[r_1^{m'}r_2^l\mathscr{I}_{nn'}^{(m+l')}(r_1\,|\,r_2)+r_1^{l'}r_2^l\mathscr{I}_{nn'}^{(m+m')}(r_1\,|\,r_2) + r_1^{m'}r_2^m\mathscr{I}_{nn'}^{(l+l')}(r_1\,|\,r_2)+r_1^{l'}r_2^m\mathscr{I}_{nn'}^{(l+m')}(r_1\,|\,r_2)]\ . \tag{4.2b}$$

Here the basic integral is

$$\mathscr{I}_{nn'}^{(p)}(r_1\,|\,r_2)\equiv(4\pi)^{-3}\int e^{-2\gamma r_3}r_{13}^nr_{23}^{n'}r_3^p\,d\Omega_1\,d\Omega_2\,d^3r_3\ . \tag{4.3}$$

For n and/or n' odd the integral would appear to be quite intractable. But in fact it is not; using the expansion of Sack[7]

$$r_{ij}^n=\sum_{\lambda=0}^{\infty}F_\lambda^{(n)}(r_i,r_j)P_\lambda(\cos\theta_{ij})\ , \tag{4.4}$$

which for n odd is itself infinite, one finds in integrating (4.3) over the spherical angles Ω_1 and Ω_2 that only the $\lambda=\lambda'=0$ term survives:

$$\mathscr{I}_{nn'}^{(p)}(r_1\,|\,r_2)=\int_0^\infty e^{-2\gamma r_3}F_0^{(n)}(r_1,r_3)\times F_0^{(n')}(r_2,r_3)r_3^{p+2}dr_3\ . \tag{4.5}$$

The $F^{(n)}$ are *terminating* hypergeometric series[8]

$$F_0^{(n)}(r_i,r_j)=r_>^nF\left[-\frac{n}{2},-\frac{(n+1)}{2};\tfrac{3}{2};(r_<\,|\,r_>)^2\right], \tag{4.6}$$

where as usual $r_<$ ($r_>$) means the lesser (greater) of r_i and r_j.

The integral in (4.5) naturally divides into three regions ($r_3\le r_<$, $r_<\le r_3\le r_>$, and $r_><r_3$) each of which can be done analytically. An example of a specific result is

$$\mathscr{I}_{01}^{(0)}(r_1\,|\,r_2)=\frac{1}{4\gamma^5r_>}\{[1+(\gamma r_>)^2]-e^{-2\gamma r_>}(1+\tfrac{1}{2}\gamma r_>)\}\ . \tag{4.7}$$

However, the number of terms rapidly increases with the size of the indices n,n' and the expressions depend on r_1 and r_2 in addition to $r_<$, $r_>$. We might point out that quadratures like (4.5) are ideally suited to analytic machine programs such as MACSYMA.

The presence of $r_<$, $r_>$ in K means that the integral equation for the v_α, Eq. (2.13), cannot be analytically solved, at least not as easily or in the same way as for a configuration-interaction kernel. Even if it could be so solved, it is not clear—given the complexity of the kernel—that it would be worthwhile to do so. We therefore offer the Rayleigh-Ritz variational principle instead.

$$\delta\left\{\frac{\langle v_\alpha K v_\alpha\rangle}{\langle v_\alpha, v_\alpha\rangle}\right\}=0\ . \tag{4.8}$$

The variational principle can be used to generate a set of analytical approximations or numerical values over a grid of the eigenfunctions $v_\alpha(r)$ (together with their associated eigenvalues λ_α). Indeed from the point of view of numerical calculation, one can go back to the defining integral equation (2.13), and straightforwardly convert it to—and solve it as—a matrix eigenvalue problem. This approach is particularly relevant to the Hylleraas-type ϕ_0, where the kernel $K(r_1\,|\,r_2)$ is now known explicitly, so that it can readily be evaluated at any desired mesh in r_1 and r_2.

Whether variationally or numerically determined, the $v_\alpha(r)$ can be used in further calculations of QHQ and/or the optical potential. In these contexts the question of idempotency becomes germane; we deal with it in Sec. V.

V. IDEMPOTENCY

In its simplest terms, the question of idempotency concerns whether the operators P and Q derived in Eqs. (2.19) are such that $P^2=P$ and $Q^2=Q$. Since the forms of the operators are given, one can square them and directly test for idempotency. We shall do that below, but note that the Feshbach theory starts with the form of $P\Psi$, Eq. (2.5), and not with P itself. In that sense it is clear from the foregoing derivation that

$$P^2\Psi=P\Psi \tag{5.1}$$

and

$$QP\Psi=0\ . \tag{5.2}$$

However, the question of idempotency of the operators themselves arises in calculations of the resonant eigenspectrum via QHQ, for that calculation is usually effected through the variational principle

$$\delta\left\{\frac{\langle\Phi QHQ\Phi\rangle}{\langle Q\Phi, Q\Phi\rangle}\right\}=0\ . \tag{5.3}$$

Here the form of Φ is arbitrary, so that $Q^2\Phi=Q\Phi$ does not necessarily hold. Furthermore, since the optical potential

$$\mathscr{V}_{\rm op}=PHQ\frac{1}{E-QHQ}QHP \tag{5.4a}$$

is generally expanded in terms of eigenfunctions of QHQ,

$$\mathscr{V}_{\rm op}=\sum_n PHQ\Phi_n\rangle\frac{1}{E-\mathscr{E}_n}\langle\Phi_n QHP\ , \tag{5.4b}$$

it would appear that a lack of idempotency would affect $\mathscr{V}_{\rm op}$ itself. In fact, the operators P and Q are *not* formally idempotent. To simplify, let us write projection operator P from (2.19) as

$$P=\sum_{i=1}^{N+1}P_i\ , \tag{5.5}$$

where

$$P_i=p(i)+\sum_n{}'\,q_n(i,i)(\lambda_n-1)^{-1}\ , \tag{5.6a}$$

$$p(i)\equiv\psi_0(r^{(i)})\rangle\langle\psi_0(r^{(i)})\ , \tag{5.6b}$$

$$q_n(i,j)\equiv(-1)^{p_i+p_j}v_n(r_i)\psi_0(r^{(i)})\rangle\langle v_n(r_j)\psi_0(r^{(j)})\ . \tag{5.6c}$$

We show in Appendix A that P^2 can be written

$$P^2=P+\sum_n{}'\frac{\lambda_n}{(\lambda_n-1)^2}\left[\sum_i q_n(i,i)-\frac{1}{N}\sum_{j=1}^{N}\sum_{\substack{i=1\\ i\neq j}}^{N}q_n(i,j)\right]\ . \tag{5.7}$$

The presence of the $(\sum'_n)$ sum shows that the P operator is not formally idempotent. [And since $Q=1-P$, it follows that $Q^2\neq Q$ and $QP\neq 0$, the deviation in both cases being the same sum in (5.7).]

However, the essential point is that matrix elements between (anti-) symmetric, quadratically integrable, but otherwise arbitrary functions of the difference term are zero. To demonstrate that, we show that matrix elements of P^2-P are zero. If Φ_a and Φ_b are completely antisymmetric, one writes from (5.6c)

$$\langle\Phi_a q_n(i,j)\Phi_b\rangle=(-1)^{p_i+p_j}\langle\Phi_a v_n(r_i)\psi_0(r^{(i)})\rangle\times\langle v_n(r_j)\psi_0(r^{(j)})\Phi_b\rangle\ .$$

Interchanging $i\leftrightarrow j$ in the second factor, whose coordinates on the one hand are dummy variables, but on the other hand, by virtue of the antisymmetry of Φ_b,

$$\Phi_b(j,j+1,\ldots,j-1)=(-1)^{p_i+p_j}\Phi_b(i,i+1,\ldots,i-1)\ ,$$

shows that Φ_b requires a second $(-1)^{p_i+p_j}$ to be brought into the appropriate order; i.e.,

$$\langle\Phi_a q_n(i,j)\Phi_b\rangle=(-1)^{2(p_i+p_j)}\langle\Phi_a v_n(r_i)\psi_0(r^{(i)})\rangle\times\langle\psi_0(r^{(i)})v_n(r_i)\Phi_b\rangle\ .$$

Thus

$$\left\langle\Phi_a\left|\frac{1}{N}\sum_{j=1}^{N}\sum_{\substack{i=1\\ i\neq j}}^{N}q_n(i,j)\right|\Phi_b\right\rangle=N\frac{1}{N}\left\langle\Phi_a\left|\sum_i q_n(i,i)\right|\Phi_b\right\rangle\ ,$$

and using this in (5.7) leads to the final result

$$\langle\Phi_a P^2\Phi_b\rangle=\langle\Phi_a P\Phi_b\rangle\ . \tag{5.8}$$

It is clear, since $Q=1-P$ as an operator, that matrix elements of Q^2 are likewise equal to those of Q, and that matrix elements of PQ (or QP) are zero. We have verified these properties numerically using our explicit open-shell projection operators and a variational form of Φ:

$$\Phi_a = \sum_{(i,j,k)\ \text{cyclic}} [e^{-(\xi r_i+\eta r_j)} r_i^l r_j^m + (i \leftrightarrow j)] \times r_k^n e^{-\zeta r_k} \chi(i,j;k)$$

and

$$\Phi_b = \Phi_a(\xi,\eta,\zeta \rightarrow \xi',\eta',\zeta';l,m,n \rightarrow l',m',n') .$$

The calculations were done for various values of the parameters $[\xi(\xi'),\eta(\eta'),\zeta(\zeta')]$ and of the powers $[l(l'), m(m'),n(n')]$. In all cases the results confirm (5.8) to the accuracy of the machine. The analysis for this test will be the basis of future calculation of *QHQ* from which we would expect to achieve even greater reliability than with quasiprojectors[8] for autoionization states of He^- and its isoelectronic counterparts.

The same considerations also apply to the optical potential, so that we may replace P and Q by any powers of P and Q without changing $\mathscr{V}_{\text{op}}$ [cf. (5.4b)]. Unfortunately, the effective idempotency of P and Q does not solve all problems here, for in the equation derived from $\langle \psi_0 \mathscr{V}_{\text{op}} \Psi \rangle$, because of the approximate nature of target state ϕ_0, to which one is calculationally constrained, the effective interaction *QHP* may allow some spurious amount of unshielded Coulomb potential to survive asymptotically, and that will ultimately cause a logarithmic divergence in the phase shifts one obtains (as the number of basis functions $n_{\max} \rightarrow \infty$). We have in fact reported on such nonconvergence[9] in calculations based on a closed shell ϕ_0 (which automatically renders the optical potential that is formally obtained from quasiprojection operators idempotent). This shows that this problem with $\mathscr{V}_{\text{op}}$ is not related to the simple idempotency of P and Q; we are now addressing ourselves to its solution.

For the present, therefore, the chief use that we envision for these operators is in resonance calculations (position, width, etc.). In this context the chief benefit that such operators should afford, in addition to increased accuracy, is the complete elimination of spurious states. The latter can arise in using quasiprojection operators.[4,5] The generalization of the present operators to the inelastic domain in Appendix B is very relevant in this respect also.

APPENDIX A

We shall sketch here the derivation of (5.7) from (5.5). By direct substitution:

$$P^2 = \sum_i \left[p(i) + \sum_n{}' \frac{q_n(i,i)}{\lambda_n - 1} \right] \sum_j \left[p(j) + \sum_m{}' \frac{q_m(j,j)}{\lambda_m - 1} \right] . \tag{A1}$$

The products which arise in this multiplication and their reduction are now indicated. Using

$$\langle \psi_0(r^{(i)}) \psi_0(r^{(i)}) \rangle = 1 \tag{A2}$$

find

$$p^2(i) = p(i) .$$

From (2.12), (2.15), and (5.6c),

$$p(i)p(j) = \frac{(-1)^{p_i+p_j+1}}{N} \times \sum_\alpha \frac{\psi_0(r^{(i)}) v_\alpha(r_i) \rangle \langle \psi_0(r^{(j)}) v_\alpha(r_j)}{\lambda_\alpha}$$

$$= -\frac{1}{N} \sum_\alpha \frac{q_\alpha(i,j)}{\lambda_\alpha} (1-\delta_{ij}) . \tag{A3}$$

From the definition of K and q, Eqs. (2.12), (2.15), and (5.6c), one can show

$$q_n(i,i)p(j) = \frac{(-1)^{p_i+p_j}}{(-N)} \psi_0(r^{(i)}) v_n(r_i) \rangle \langle K(i \mid j) v_n(r_i) \rangle \langle \psi_0(r^{(j)})$$

$$= \psi_0(r^{(i)}) \left[\frac{(-1)^{p_i+p_j+1}}{N\lambda_n} v_n(r_i) \rangle \langle v_n(r_j) \psi_0(r^j) \right]$$

$$= -\frac{1}{N} \frac{q_n(i,j)}{\lambda_n} (1-\delta_{ij}) + q_n(i,i)\delta_{ij} . \tag{A4}$$

Similarly

$$p(i)q_m(j,j) = -\frac{1}{N} \frac{q_m(i,j)}{\lambda_m} (1-\delta_{ij}) + q_m(i,i)\delta_{ij} . \tag{A5}$$

Finally, using the same equations,

$$q_n(i,i)q_m(j,j) = \psi_0(r^{(i)}) v_n(r_i) \rangle \langle \psi_0(r^{(i)}) v_n(r_i) \delta_{ij}\delta_{nm}$$

$$+ (1-\delta_{ij}) \psi_0(r^{(i)}) v_n(r_i) \rangle \left\langle v_n(r_i) \frac{(-1)^{p_i+p_j} K(i \mid j)}{-N} v_m(r_j) \right\rangle \langle \psi_0(r^{(j)}) v_m(r_j)$$

$$= q_n(i,i)\delta_{ij}\delta_{nm} - \frac{q_n(i,j)(1-\delta_{ij})\delta_{nm}}{\lambda_n N} . \tag{A6}$$

Substituting these products into (A1) gives

$$P^2=\sum_i\sum_j\left[p(i)\delta_{ij}+\sum_n{}'\left[-\frac{q_n(i,j)}{N\lambda_n}(1-\delta_{ij})-\frac{2}{N}\frac{q_n(i,j)(1-\delta_{ij})}{\lambda_n(\lambda_n-1)}+\frac{2q_n(i,j)\delta_{ij}}{\lambda_n-1}+\frac{q_n(i,j)\delta_{ij}}{(\lambda_n-1)^2}-\frac{1}{N}\frac{q_n(i,j)(1-\delta_{ij})}{\lambda_n(\lambda_n-1)^2}\right]\right]$$

$$=\sum_i\left[p(i)+\sum_n{}'q_n(i,i)\left[\frac{2}{\lambda_n-1}+\frac{1}{(\lambda_n-1)^2}\right]\right]+\sum_i\sum_{\substack{j\\ j\neq i}}\left[\left[-\frac{1}{N}\right]\sum_n{}'q_n(i,j)\left[\frac{2}{\lambda_n(\lambda_n-1)}+\frac{1}{\lambda_n}+\frac{1}{\lambda_n(\lambda_n-1)^2}\right]\right]$$

$$=\sum_i\left[\left[p(i)+\sum_n{}'\frac{q_n(i,i)}{\lambda_n-1}\right]+\sum_n{}'\frac{q_n(i,i)\lambda_n}{(\lambda_n-1)^2}\right]-\frac{1}{N}\sum_i\sum_{\substack{j\\ j\neq i}}\sum_n{}'\frac{q_n(i,j)\lambda_n}{(\lambda_n-1)^2}$$

$$=P+\sum_n{}'\frac{\lambda_n}{(\lambda_n-1)^2}\left[\sum_i q_n(i,i)-\frac{1}{N}\sum_i\sum_{\substack{j\\ j\neq i}}q_n(i,j)\right] \tag{A7}$$

Q.E.D.

APPENDIX B

In this appendix we generalize the form of the "projection" operators needed to deal with resonances in the inelastic domain. The generalized $P\Psi$ is defined to be

$$P\Psi\equiv\sum_{i=1}^{N+1}(-1)^{p_i}\sum_{\nu=0}^{n}u_\nu(r_i)\psi_\nu(r^{(i)})\ , \tag{B1}$$

where ψ_ν are the generalized channel functions and the number of open channels is assumed to be $n+1$ (i.e., $\nu=0,1,2,\ldots,n$):

$$\psi_\nu(r^{(i)})=\sum(L_\nu l_\nu M_\nu m_\nu\,|\,LM)\times(s_\nu\tfrac{1}{2}M_{S\nu}m_{s\nu}\,|\,SM_S)\times\phi_\nu(x^{(i)})Y_{l_\nu m_\nu}(\Omega_i)\chi_{1/2\,m_s}(i)\ . \tag{B2}$$

The summation in (B2) is over scattered particle indices $(m_\nu,m_{s\nu})$ and target magnetic quantum numbers $(M_\nu,M_{s\nu})$ that are consistent with the total quantum numbers L,M of the total partial wave. (The total scattering wave function is a sum over partial waves, but as usual partial waves are uncoupled and each is handled separately; the labels L and M on Ψ are suppressed.)

In general there may be several l_ν (with associated spin indices $\frac{1}{2}$, $m_{s\nu}$) that can couple to form a given L, S for a given ν. They will give rise to a multiplicity of eigenphase shifts σ_ν (including Coulomb parts if the target is charged), which are manifested in the asymptotic form of the radial eigenfunctions:

$$\lim_{r_i\to\infty}u_\nu(r_i)=\frac{\sin(k_\nu r_i-\pi l_\nu/2+\sigma_\nu)}{k_\nu r_i}\ . \tag{B3}$$

The degeneracy due to such eigenchannels will not be explicitly exhibited here.

The P operator is, in analogy to (2.9), deduced from the conditions

$$\langle\psi_\nu(r^{(i)})Q\Psi\rangle_{r^{(i)}}=0\ , \tag{B4}$$

where by definition $Q=1-P$. Using (B1) in (B4) leads to the equations

$$w_\nu(r_i)=u_\nu(r_i)-\sum_{\mu=0}^{n}\langle K_{\nu\mu}(r_i\,|\,r_j)u_\mu(r_j)\rangle_{r_j}\ , \tag{B5}$$

where

$$w_\nu(r_i)\equiv(-1)^{p_i}\langle\psi_\nu(r^{(i)})\Psi\rangle_{r^{(i)}} \tag{B6}$$

and

$$K_{\nu\mu}(r_i\,|\,r_j)\equiv(-1)^{p_i+p_j+1}N\langle\psi_\nu(r^{(i)})\psi_\mu(r_j)\rangle_{r^{(ij)}}\ . \tag{B7}$$

(The range of μ is the same as that of ν.) The main aspect of this generalization is the fact that the kernels $K_{\nu\mu}(r_i\,|\,r_j)$ form a matrix in ν,μ.

To proceed further, let us define the vectors $\mathbf{u}$ and $\mathbf{w}$:

$$\mathbf{u}=\begin{bmatrix}u_0\\ u_1\\ \vdots\\ u_n\end{bmatrix}\ ,\quad \mathbf{w}\equiv\begin{bmatrix}w_0\\ w_1\\ \vdots\\ w_n\end{bmatrix}\ . \tag{B8}$$

Equation (B5) may be reexpressed

$$\mathbf{w}=\mathbf{u}-\langle\underline{K}\mathbf{u}\rangle_{r_j}\ , \tag{B5'}$$

where $\underline{K}$ is the matrix $K_{\mu\nu}$ given by (B7). We now define an auxiliary spectrum of vector $\mathbf{v}_\alpha$ to satisfy a matrix eigenvalue problem

$$\mathbf{v}_\alpha=\lambda_\alpha\langle\underline{K}\mathbf{v}_\alpha\rangle\ . \tag{B9}$$

[We call the number of eigensolutions of (B9) n_λ.] In complete analogy to (2.14) and (2.15), one can show

$$\langle\mathbf{v}_\alpha\cdot\mathbf{v}_\beta\rangle=\delta_{\alpha\beta}\ . \tag{B10}$$

In (B9) and (B10) dot products mean scalar products over channel indices:

$$\langle\mathbf{v}_\alpha\cdot\mathbf{v}_\beta\rangle\equiv\sum_{\mu=0}^{n}\langle v_\mu^{(\alpha)}v_\mu^{(\beta)}\rangle\ ,$$

$$\langle\mathbf{K}\mathbf{v}_\alpha\rangle\equiv\sum_{\nu=0}^{n}\langle K_{\mu\nu}v_\nu^{(\alpha)}\rangle\ ,$$

where for convenience we have written $(\mathbf{v}_\alpha)_\nu\equiv v_\nu^{(\alpha)}$, etc. In

analogy to (2.15) we can expand $\underline{K}$ in the vector space defined by the $\mathbf{v}_\beta\rangle$:

$$\underline{K}(r_1\,|\,r_2)=\sum_{\beta=1}^{n_\lambda}\frac{\mathbf{v}_\beta(r_1)\rangle\langle\mathbf{v}_\beta(r_2)}{\lambda_\beta}\ . \tag{B11}$$

Thus (B5′) reduces down to (in ket form)

$$\mathbf{w}\rangle=\mathbf{u}\rangle-\sum_\beta\frac{\mathbf{v}_\beta\rangle\langle\mathbf{v}_\beta\cdot\mathbf{u}\rangle}{\lambda_\beta}\ . \tag{B12}$$

From (B12), premultiplying by $\langle\mathbf{v}_\alpha$ and using the orthnormality, (B10), one can derive ($\lambda_\alpha\neq1$)

$$\langle\mathbf{v}_\alpha\cdot\mathbf{u}\rangle=\frac{\lambda_\alpha}{\lambda_\alpha-1}\langle\mathbf{v}_\alpha\cdot\mathbf{w}\rangle\ , \tag{B13}$$

where again the $\lambda_\alpha=1$ will play no role. Omitting it, we can reexpress (B12) in the form

$$\mathbf{u}\rangle=\mathbf{w}\rangle+{\sum_{\lambda_\alpha}}'\frac{\mathbf{v}_\alpha\rangle\langle\mathbf{v}_\alpha\cdot\mathbf{w}\rangle}{\lambda_\alpha-1}\ . \tag{B14}$$

Equation (B14) is the desired generalization of (2.16), and from it we can obtain the explicit form of the P operator. Let us premultiply (B1) by any specific $\langle\psi_\nu$ of the channel wave functions $\boldsymbol{\psi}_0$:

$$\boldsymbol{\psi}_0\equiv\begin{bmatrix}\psi_0\\ \psi_1\\ \vdots\\ \psi_n\end{bmatrix}\ . \tag{B15}$$

From (B1) and (B14) we have

$$\langle\psi_\nu P\Psi\rangle_{r^{(i)}}=\langle\psi_\nu(r^{(i)})\,|\sum_{j=1}^{N+1}(-1)^{p_j}\left[\mathbf{w}(r_j)\psi_0\rangle+{\sum_{\lambda_\alpha}}'\frac{\mathbf{v}_\alpha\cdot\boldsymbol{\psi}_0\rangle\langle\mathbf{v}_\alpha\cdot\mathbf{w}\rangle}{\lambda_\alpha-1}\right]. \tag{B16}$$

[On the rhs of (B16) it is apparent that we have also used ket notation.] Inserting now the definition of $\mathbf{w}$ from (B6), which in vector form is

$$\mathbf{w}(r_j)=(-1)^{p_j}\langle\boldsymbol{\psi}_0\Psi\rangle_{r^{(j)}}\ , \tag{B6′}$$

into (B16) gives

$$\langle\psi_\nu(r^{(i)})P\Psi\rangle_{r^{(i)}}=\langle\psi_\nu\,|\sum_{j=1}^{N+1}(-1)^{p_j}\left[\boldsymbol{\psi}_0\rangle\cdot(-1)^{p_j}\langle\boldsymbol{\psi}_0\Psi\rangle+\sum_{\lambda_\alpha}\mathbf{v}_\alpha\cdot\boldsymbol{\psi}_0\rangle(-1)^{p_j}\langle\mathbf{v}_\alpha\cdot\boldsymbol{\psi}_0\Psi\rangle\right].$$

We rewrite the rhs of the above so that the ket $\Psi\rangle$ is the right-most factor:

$$\langle\psi_\nu(r^{(i)}P\Psi\rangle_{r^{(i)}}=\langle\psi_\nu\,|\sum_{j=1}^{N+1}\left[\boldsymbol{\psi}_0\rangle\cdot\langle\boldsymbol{\psi}_0+{\sum_{\lambda_\alpha}}'\frac{\mathbf{v}_\alpha\cdot\boldsymbol{\psi}_0\rangle\langle\mathbf{v}_\alpha\cdot\boldsymbol{\psi}_0}{\lambda_\alpha-1}\right]\Psi\rangle_{r^{(i)}}\ . \tag{B17}$$

At this point, we can compare the lhs and rhs of (B17) to allow the desired generalization of the P operator to be read off:

$$P=\sum_{j=1}^{N+1}\left[\boldsymbol{\psi}_0(r^{(j)})\rangle\cdot\langle\boldsymbol{\psi}_0(r^{(j)})+{\sum_{\lambda_\alpha}}'\frac{\mathbf{v}_\alpha(r_j)\cdot\boldsymbol{\psi}_0(r^{(j)})\rangle\langle\mathbf{v}_\alpha(r_j)\cdot\boldsymbol{\psi}_0(r^{(j)})}{\lambda_\alpha-1}\right] \tag{B18a}$$

or in the explicit form of sums over eigenchannels

$$P=\sum_{j=1}^{N+1}\left[\sum_{\nu=0}^{n}\psi_\nu\rangle\langle\psi_\nu+{\sum_{\lambda_\alpha}}'\frac{\left[\sum_\nu v_\nu^{(\alpha)}\psi_\nu\rangle\right]\left[\sum_\mu\langle v_\mu^{(\alpha)}\psi_\mu\right]}{\lambda_\alpha-1}\right]. \tag{B18b}$$

We repeat that the explicit form of the Q operator can be obtained from $Q=P-1$. It should be noted from (B18) that P and Q contain terms of the form $v_\nu^{(\alpha)}\psi_\nu\rangle\langle v_\mu^{(\alpha)}\psi_\mu$ in which $\mu\neq\nu$; thus these operators are not trivial extensions of the elastic projection operators. To our knowledge, the above inelastic generalizations of P and Q operator have not previously been given. We are grateful to Dr. Alexander Berk for assistance with this analysis.

As a final item it is noted that the number of exceptions to the basic conditions (B4) that can occur when quasiprojectors $\hat{Q}$ are used in place of Q is by definition the number of spurious eigenvalues which the $\hat{Q}$ allows.[4,5] Since by definition the operator Q allows no exceptions, *it follows that the spectrum of QHQ will have no spurious eigenvalues.* This is justification of the assertion made in the last paragraph of Sec. V.

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