Compound-Atom States for Two-Electron Systems*

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The energies of the lowest He-like compound-atom or resonance states lying below the $n=2$ hydrogenic level are evaluated variationally for He and H⁻. In order to do this, we employ the definition of such states given by Feshbach as eigenvalues of the Hamiltonian with the open channel projected out, together with the modification required by the Pauli principle. Our trial wave function uses a Legendre expansion in the relative angle and a sum of exponentials in the radial coordinates, with appropriate angular factors to obtain the desired symmetry, parity, and orbital-angular-momentum eigenvalues associated with the $^{1,3}S^e$ and $^{1,3}P^o$ states. Our results are approximations to the actual physical resonances in that the shift and finite width caused by coupling to the neighboring continuum are not included. It appears, however, that the actual shifts are small, so that the positions of these compound-atom states are believed to give a close indication of where the physical resonances may be expected to occur. The results for He and H⁻ are compared in detail with the calculations of resonances in e-H and e-He⁺ elastic scattering and with the observation of these states by ultraviolet photon absorption in He (where they are called autoionizing levels) and by inelastic scattering of electrons from He.

I. INTRODUCTION

THE existence of states of compound nuclei made up of an excited target nucleus and an incident nucleon has long been known to give rise to the strong resonances found in nucleon-nucleus elastic scattering. The theory of such states would lead one to believe that they should just as well exist in the scattering of electrons by atoms. However, lack of detailed experimental data for the elastic scattering of monoenergetic electrons by atoms resulted in a lack of interest in the properties of such compound atom states. Certainly, there was an awareness of the possible existence of such resonance states as an explanation of the phenomenon of autoionization, which was postulated to explain certain long known anomalous features of the continuous absorption of radiation by atoms.

In recent years, interest has been revived in the subject of these compound atom states as a result of advances in theoretical and experimental techniques. Burke and Schey,[1] in the course of a detailed close-coupling calculation on electron-hydrogen elastic scattering, found a number of resonances occurring just below the inelastic $n=2$ threshold. Very recently Burke, McVicar, and Smith[2] have found resonances in a similar calculation of e−He⁺ elastic scattering. Inelastic scattering of electrons[3] by He showed discrete energy losses of about 60 eV, which were interpreted

by Fano[4] as the excitations of compound levels of the He atom, which interact with the adjacent continuum. Additional energy loss experiments in He by Simpson, Mielczarek, and Cooper,[5] using electron beams with very sharp energy resolution have disclosed the presence of other compound levels lying between 60 and 65.4 eV, the threshold for single ionization with the He⁺ left in the $n=2$ state. Finally, the continuous optical absorption measurements of Madden and Codling[6] clearly exhibited an entire Rydberg series of the compound (or autoionization) states in He.

In the present work, we follow the method of Feshbach[7] in describing resonant scattering of a particle by a composite system. The presence of resonances is manifested by the existence of singularities in the generalized optical potential for the system, and the energies at which these singularities occur are seen to be the eigenvalues of an altered Hamiltonian. These are our compound atom or resonance states. The relation of these states to resonance reactions in inelastic processes, derived by Fano by means of configuration interactions between the discrete states and the continuum, is also seen to follow from Feshbach's approach. We follow the method of Hahn, O'Malley, and Spruch[8] in the treatment of identical particles (electron on H-like target).

We are left with a Rayleigh-Ritz variational calculation for the energies of the compound states, which we perform with the choice of an appropriate trial function. Finally, a detailed comparison of our variational esti-

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mates of the energy levels is made with existing experimental data and other theoretical results.

II. THEORY OF COMPOUND ATOM STATES AND RESONANCE REACTIONS

In this section, we attempt to summarize the theory of the compound atom or resonance states and their relation to resonance scattering and reactions, using the approach developed by Feshbach.[7]

We begin with the Schrödinger equation for a fixed hydrogen-like system and an incident electron

$$(H-E)\Psi(\mathbf{r}_1,\mathbf{r}_2)=0, \tag{1}$$

where it is understood that Ψ is also an eigenfunction of the total L^2, L_z, and parity of the two-electron system. Full antisymmetry in space and spin coordinates is achieved by requiring $\Psi(\mathbf{r}_1,\mathbf{r}_2)$ to be symmetric for singlet states and antisymmetric for triplet states. The asymptotic form for the case of scattering at energies below the inelastic threshold is

$$\Psi(\mathbf{r}_1,\mathbf{r}_2) \underset{r_2\to\infty}{\longrightarrow} u_0(\mathbf{r}_1)Y_{LM}(\hat{\mathbf{r}}_2)[\sin(kr_2-\tfrac{1}{2}L\pi+\eta_L)/kr_2], \tag{2}$$

which thus designates 1 as the target electron and 2 as the incident electron, since u_0 is the hydrogenic ground-state wave function. For $Z>1$, the phase in (2) must be suitably modified, because of the long-range Coulomb interaction.

Following Feshbach[7] and Hahn, O'Malley, and Spruch[8] we introduce a pair of projection operators P and Q, which originally satisfy only

$$P+Q=1 \tag{3}$$

and the intrinsic property of projection operators

$$P^2=P, \quad Q^2=Q. \tag{4}$$

This allows us to obtain the coupled equations

$$P(H-E)(P+Q)\Psi=0, \tag{5a}$$

$$Q(H-E)(P+Q)\Psi=0. \tag{5b}$$

These are formally uncoupled by solving (5b) for

$$Q\Psi=[1/Q(E-H)Q]QHP\Psi \tag{6}$$

and putting this into (5a), to give

$$P[H+HQ[1/Q(E-H)Q]QH-E]P\Psi=0, \tag{7}$$

where we make use of conditions that Q and P project out orthogonal parts of Hilbert space, or $QP=PQ=0$, which follows from (3) and (4).

We have not as yet specified the form of projection operators P and Q, other than that they satisfy (3) and (4). We choose them so that (a) they are symmetric in $\mathbf{r}_1$ and $\mathbf{r}_2$, since we are dealing with two identical particles, and (b) $P\Psi$ gives the correct asymptotic behavior (2) for energies below the inelastic threshold,

i.e.,

$$P\Psi \underset{r_1 \text{ or } r_2\to\infty}{\longrightarrow} \Psi. \tag{8}$$

Thus, even though $P\Psi$ differs from the total Ψ over all finite regions of space, since its asymptotic behavior is identical to that of the total Ψ, the solution of (7) for $P\Psi$ will lead to the exact scattering cross section. Another important consequence of (b) is that the component $Q\Psi$ vanishes asymptotically and hence belongs to Hilbert space.

A pair of projection operators satisfying all of the above requirements is given by Hahn, O'Malley, and Spruch,[8] i.e.,

$$\begin{aligned} Q&=Q_1Q_2,\\ P&=1-Q, \end{aligned} \tag{9}$$

where $Q_i=1-P_i$ and P_i is the operator[9] which projects out the hydrogenic ground state in the ith electron coordinates, $|u_0(\mathbf{r}_i)\rangle\langle u_0(\mathbf{r}_i)|$. One can easily show that this choice of P and Q satisfies all the above requirements. For example, if we expand the true wave function in terms of the complete set of hydrogenic wave functions, then

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=\left(\sum_n+\int\right)u_n(\mathbf{r}_1)F_n(\mathbf{r}_2), \tag{10}$$

and

$$\begin{aligned} P\Psi&=u_0(\mathbf{r}_1)F_0(\mathbf{r}_2)+u_0(\mathbf{r}_2)\langle u_0(\mathbf{r}_2)|\Psi\rangle\\ &\quad-u_0(\mathbf{r}_1)u_0(\mathbf{r}_2)\langle u_0(\mathbf{r}_2)|F_0(\mathbf{r}_2)\rangle \underset{r_2\to\infty}{\longrightarrow} u_0(\mathbf{r}_1)F_0(\mathbf{r}_2), \end{aligned}$$

where $F_0(\mathbf{r}_2)$ has the asymptotic form indicated in (2). If one were interested in the scattering when excitation is possible, i.e., the multichannel case, this choice of P and Q would no longer be appropriate.[9]

Since $F_0(\mathbf{r}_2)$ contains all of the essential elastic scattering information, one could rewrite (7) in the form of a one-body integro-differential equation for $F_0(\mathbf{r}_2)$, where all the two-body effects are contained in a generalized optical potential. It would, however, be very complicated and not susceptible to direct solution.

We now follow the procedure of Feshbach[7] in describing the appearance of resonances. They will arise from the presence of zeros in the denominator of the generalized optical potential. The basic equation (7) may be rewritten, using the fact that $P=P^2$, as

$$[H_{PP}+V_{\text{opt}}-E]P\Psi=0, \tag{11}$$

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[9] This choice of P_i is the appropriate one for dealing with compound levels below the $n=2$ threshold. If one were interested in the compound levels below the hydrogenic state of arbitrary n, the appropriate forms are

$$P_i^{(n)}=\sum_{n'=1}^{n-1}\sum_{l'=0}^{n'-1}\sum_{m'=-l'}^{l'}|u_{n'l'm'}(\mathbf{r}_i)\rangle\langle u_{n'l'm'}(\mathbf{r}_i)|,$$

and, as above, $Q_i^{(n)}=1-P_i^{(n)}$, $Q^{(n)}=Q_1^{(n)}Q_2^{(n)}$, and $P^{(n)}=1-Q^{(n)}$. This general choice of $Q^{(n)}$ will lead to a spectrum for $Q^{(n)}HQ^{(n)}$ whose continuum starts at the nth level. In the present paper, $n=2$ throughout, and this superscript has been dropped. Also, for convenience, u_0 is used for u_{100}.

where

$$H_{PP} = PHP, \quad V_{\text{opt}} = PHQ[1/Q(E-H)Q]QHP.$$

The explicit appearance of the resonance energies comes about by introducing the complete set of eigenfunctions for the operator $QHQ = H_{QQ}$, i.e.,

$$H_{QQ}\Phi_n(\mathbf{r}_1, \mathbf{r}_2) = \mathcal{E}_n \Phi_n. \quad (12)$$

Now, while the operators H and also H_{PP} have a spectrum which is continuous in the scattering region, it is a consequence[8] of the choice of Q, following from Eq. (8), that the eigenvalues $\mathcal{E}_n$ of H_{QQ} are discrete point eigenvalues below the excitation threshold. These eigenstates Φ_n are interpreted, as shown below, as states of the compound atom or resonance states. It follows from (12) that $Q\Phi_n = \Phi_n$, so that the set of Φ_n are also eigenfunctions of Q with eigenvalues 1. The completeness of the set Φ_n in the Q subspace allows us to insert

$$Q = \sum_n |\Phi_n\rangle\langle\Phi_n|$$

into the expression for V_{opt} immediately following $1/Q(E-H)Q$. We make use of the theorem stating that when a function containing operators operates on an eigenfunction of these operators, one may replace the operators by their respective eigenvalues, or

$$[1/Q(E-H)Q]|\Phi_n\rangle = [1/(E-\mathcal{E}_n)]|\Phi_n\rangle. \quad (13)$$

In the case where resonances may be considered as isolated, which appears to be so for electron-atom collisions, the total optical potential may be divided into two parts when E is close to one of the $\mathcal{E}_n$'s, say $\mathcal{E}_s$, giving (11) in the form

$$(H'-E)P\Psi = -\frac{H_{PQ}|\Phi_s\rangle\langle\Phi_s|H_{QP}}{E-\mathcal{E}_s}P\Psi, \quad (14)$$

where

$$H' = H_{PP} + \sum_{n \neq s} \frac{H_{PQ}|\Phi_n\rangle\langle\Phi_n|H_{QP}}{E-\mathcal{E}_n}$$

is the slowly varying (in energy) part of the Hamiltonian which gives rise to potential scattering, or the nonresonant part of the scattering. The sum is understood to include an integral over the continuous part of the spectrum.

To solve Eq. (14) we proceed as did Feshbach, except that we use the standing wave solutions for the sake of simplicity. First, consider the homogeneous solution $P\Psi_0$ of (14), satisfying

$$(H'-E)P\Psi_0 = 0, \quad (15)$$

with asymptotic form as $r_2 \to \infty$ given by Eq. (2) with η replaced by η_0. This has the interpretation of the potential scattering part of the wave function $P\Psi$. Equation (14) is now solved formally using the standing-wave Green's function G constructed from the homo-

geneous solution. G has the asymptotic form

$$G \underset{r_2 \to \infty}{\longrightarrow} -(2mk/\hbar^2)u_0(\mathbf{r}_1)Y_{LM}(\hat{\mathbf{r}}_2)$$

$$\times [\cos(kr_2 - \tfrac{1}{2}L\pi + \eta_0)/kr_2]\langle\Psi_0 P. \quad (16)$$

Again, if $Z > 1$, the appropriate Coulomb modified phase should appear in the argument of the cosine function. The formal solution of Eq. (14) is

$$P\Psi^{(u)} = P\Psi_0 + (E-\mathcal{E}_s)^{-1}GH_{PQ}\Phi_s\rangle\langle\Phi_s H_{QP}P\Psi^{(u)}\rangle, \quad (17)$$

where the superscript (u) signifies that this wave function does not necessarily have the normalization of (2). Now Eq. (17) is a separable equation for $P\Psi^{(u)}$ and can be solved exactly (given Ψ_0 and Φ_s). Multiplying Eq. (17) on the left by $\langle\Phi_s H_{QP}$, we find

$$\langle\Phi_s H_{QP}\Psi^{(u)}\rangle = \frac{\langle\Phi_s H_{QP}\Psi_0\rangle}{1-(E-\mathcal{E}_s)^{-1}\langle\Phi_s H_{QP}GH_{PQ}\Phi_s\rangle}. \quad (18)$$

Using (18), the explicit solution (17) for $P\Psi$ becomes

$$P\Psi^{(u)} = P\Psi_0 + \frac{|GH_{PQ}\Phi_s\rangle\langle\Phi_s H_{QP}\Psi_0\rangle}{E-\mathcal{E}_s-\Delta_s}, \quad (19)$$

where

$$\Delta_s = \langle\Phi_s H_{QP}GH_{PQ}\Phi_s\rangle \quad (20)$$

is the shift in the energy from $\mathcal{E}_s$ caused by the coupling to the continuum wave function Ψ_0.

Going now to the limit $r_2 \to \infty$ and using (16) for G and the asymptotic form (2) of Ψ_0, we find

$$P\Psi^{(u)} \underset{r_2 \to \infty}{\longrightarrow} u_0(\mathbf{r}_1)Y_{LM}(\hat{\mathbf{r}}_2)$$

$$\times [\sin(kr_2 - \tfrac{1}{2}L\pi + \eta_0 + \eta_r)/kr_2 \cos\eta_r], \quad (21)$$

where

$$\tan\eta_r = -\tfrac{1}{2}\Gamma_s/(E-\mathcal{E}_s-\Delta_s) \quad (22)$$

and Γ_s, the width, is given by

$$\Gamma_s/2 = (2mk/\hbar^2)|\langle\Psi_0 H_{PQ}\Phi_s\rangle|^2. \quad (23)$$

[Equation (23) differs from the standard definition[4] of the level width by the constant factor $2mk/\hbar^2\pi$. To obtain agreement, the asymptotic normalization of Ψ_0 as given in Eq. (2) should be multiplied by the square root of this factor.] We see from Eq. (21) that the total phase shift is $\eta_0 + \eta_r$, the sum of the potential and resonance phase shifts, so that (for $Z = 1$) the partial elastic-scattering cross section is given by

$$\sigma_L = (4\pi/k^2)(2L+1)\sin^2(\eta_0 + \eta_r). \quad (24)$$

From (22) it follows that the phases increase by π in going through the resonance. Assuming the width Γ_s to be small compared to the energy region in which η_0 and Ψ_0 vary appreciably, Γ_s and Δ_s are taken to be constant and evaluated at $E = \mathcal{E}_s + \Delta_s$.

Inelastic Processes

Thus far we have seen, following the method of Feshbach, how the compound states Φ_s, the eigenstates

of QHQ, give rise to resonances in elastic scattering. However, it should be clear that the resonance behavior built into the wave function in Eq. (19) will show up also in any inelastic process (involving a He-like system in the present instance, with $E \simeq \mathcal{E}_s$) having this as a final state, as for example in photoionization. The way in which the resonant state Φ_s affects the matrix element $\langle \Psi | T | i \rangle$ for the transition, through its effect on the wave function Ψ, has been derived by Fano. He uses the method of configuration interaction, treating states corresponding to Φ_s and Ψ_0 as degenerate approximate solutions of the wave equation, and using them to construct an eigenfunction Ψ.

Our solution (19) is also such an eigenfunction. Now that this wave function has been derived, it is only a short distance further to derive Fano's result for the general matrix element $\langle \Psi | T | i \rangle$ for transitions between an initial state i, and the final state Ψ. For this matrix element, the wave function Ψ is assumed to have the asymptotic normalization of Eq. (2). Our function whose P component is given by (19) has instead the asymptotic form (21), which differs from (2) by the factor $\cos\eta_r$ in the denominator. It must therefore be multiplied by $\cos\eta_r$ in order to be properly normalized. We may without loss of generality go one step further and write the properly normalized Eq. (19) in the form

$$P\Psi = \cos\eta_r P\Psi^{(u)} = \cos\eta_r P\Psi_0 - \sin\eta_r P\Psi_1. \quad (25)$$

The function $P\Psi_1$, thus defined by substituting (19) into (25), may be written using (22) and (23) as

$$P\Psi_1 = (\hbar^2/2mk)\frac{GH_{PQ}\Phi_s\rangle}{\langle \Psi_0 H_{PQ}\Phi_s\rangle}. \quad (26)$$

The significant thing about this function Ψ_1 is that, like Ψ_0, it does not contain the rapidly varying energy function $E - \mathcal{E}_s - \Delta_s$, and so may also be treated as energy-independent in going through the (assumed narrow) resonance.

Before proceeding to write the matrix element for the transition, we note that Eq. (25) contains only one component $P\Psi$ of the scattering wave function, whereas we need the entire wave function $\Psi = P\Psi + Q\Psi$. However, given $P\Psi$, then $Q\Psi$ is immediately determined by Eq. (6). It is shown in the Appendix that with $P\Psi$ given by (25), $Q\Psi$ is of the same form as (25), so that we may write for the entire scattering wave function

$$\Psi = \Psi_0 \cos\eta_r - \Psi_1 \sin\eta_r, \quad (27)$$

where Ψ_0 and Ψ_1 are given by (A7) and (A8) of the Appendix. The expressions for $\sin\eta_r$ and $\cos\eta_r$, which follow directly from (22), are

$$\sin\eta_r = \frac{\frac{1}{2}\Gamma_s}{[(E - \mathcal{E}_s - \Delta_s)^2 + (\frac{1}{2}\Gamma_s)^2]^{1/2}},$$

$$\cos\eta_r = \frac{\mathcal{E}_s + \Delta_s - E}{[(E - \mathcal{E}_s - \Delta_s)^2 + (\frac{1}{2}\Gamma_s)^2]^{1/2}}.$$

The matrix element $\langle \Psi | T | i \rangle$ now follows immediately and is given by

$$\langle \Psi | T | i \rangle = \cos\eta_r \langle \Psi_0 | T | i \rangle - \sin\eta_r \langle \Psi_1 | T | i \rangle$$
$$= [(\mathcal{E}_s + \Delta_s - E)\langle \Psi_0 | T | i \rangle - \frac{1}{2}\Gamma_s \langle \Psi_1 | T | i \rangle]/$$
$$[(E - \mathcal{E}_s - \Delta_s)^2 + (\frac{1}{2}\Gamma_s)^2]^{1/2}. \quad (28)$$

This is the general matrix element for a one-level resonance reaction. Elastic scattering is included as a special case. Away from the resonance, assuming it to be narrow, $\sin\eta_r \rightarrow 0$, and the absolute value of the matrix element for the transition is simply $|\langle \Psi_0 | T | i \rangle|$, the nonresonant matrix element. From (28) the formula derived by Fano for the ratio of the cross section to the nonresonant cross section follows immediately, namely,

$$\frac{|\langle \Psi | T | i \rangle|^2}{|\langle \Psi_0 | T | i \rangle|^2} = \frac{(\epsilon + q)^2}{1 + \epsilon^2}, \quad (29)$$

where

$$\epsilon = -\cot\eta_r \quad \text{and} \quad q = \langle \Psi_1 | T | i \rangle / \langle \Psi_0 | T | i \rangle. \quad (30)$$

We have suppressed the subscript s on η_r, ϵ, and q, it being understood that they depend on the particular resonance.

In summary then, we have seen that, given the eigenstates Φ_s, of the operator QHQ, these compound atom or resonance states give rise to Breit-Wigner-type resonances in both elastic and inelastic processes involving the state Ψ of the helium-like system when $E \simeq \mathcal{E}_s$.

In the following section, we proceed to calculate variationally the energies $\mathcal{E}_s$ of the lowest series of resonances states for the He and H$^-$ systems.

III. VARIATIONAL CALCULATION OF THE COMPOUND-ATOM ENERGY LEVELS

Our objective is to evaluate the eigenvalues of the compound system, defined in (12) as the eigenvalues of the altered Hamiltonian $H_{QQ} = QHQ$. This is as much a two-electron problem as when dealing with the ordinary two-electron Hamiltonian H, and thus we consider a variational treatment. By assuming a trial function for Φ, we may perform a Rayleigh-Ritz calculation, which will yield an upper bound on the ground-state energy associated with the operator H_{QQ}. Also the Hylleraas-Undheim theorem states that if the trial function is made up of a linear combination of n functions, then the variational procedure leads to n energy eigenvalues, each of which is an upper bound on the respective exact eigenvalue.

We can remove the Q operators from the Hamiltonian and put them into the trial function, as shown in the following. Starting with (12)

$$QHQ | \Phi_s \rangle = \mathcal{E}_s | \Phi_s \rangle, \quad (12)$$

we operate on the left with $\langle \Phi_s | Q = \langle \Phi_s | Q^2$, obtaining

$$\langle \Phi_s | QHQ | \Phi_s \rangle = \mathcal{E}_s \langle \Phi_s | Q^2 | \Phi_s \rangle$$

and by the Hermiticity of Q and QH,

$$\langle Q\Phi_s | H | Q\Phi_s \rangle = \mathscr{E}_s \langle Q\Phi_s | Q\Phi_s \rangle. \tag{31}$$

Now the normal Hamiltonian appears, but the eigenfunctions Φ_s have been replaced by $Q\Phi_s$. We take an arbitrary trial function Φ_{tr}, from which we construct

$$\phi_{tr} = Q\Phi_{tr} = (1 - P_1 - P_2 + P_1 P_2)\Phi_{tr}, \tag{32}$$

which then serves as our trial function for a conventional variational calculation. Each Φ_{tr} must have built in the correct symmetry properties for the state under consideration, i.e., eigenfunctions of L^2, L_z, parity, and symmetry in $\mathbf{r}_1 \rightleftarrows \mathbf{r}_2$ (for singlet or triplet states). It is easy to show that the operation of Q on Φ_{tr} preserves all of these properties. The effect of Q operating on an arbitrary function is seen to project out of it the ground atomic state u_0 in each of the electrons, or

$$\Phi_{tr} = \sum_{i,j \neq 0} a_{ij} u_i(\mathbf{r}_1) u_j(\mathbf{r}_2). \tag{33}$$

It has been shown[10] that the *exact* two-electron wave functions for the $^{1,3}S^e$ and $^{1,3}P^o$ states can be written in the forms

$$\Phi(^{1,3}S^e) = F(r_1, r_2, r_{12}) \pm F(r_2, r_1, r_{12}),$$

$$\Phi(^{1,3}P^o) = r_1 Y_{1M}(\hat{\mathbf{r}}_1) G(r_1, r_2, r_{12}) \pm r_2 Y_{1M}(\hat{\mathbf{r}}_2) G(r_2, r_1, r_{12}).$$

We approximate these by taking the trial function

$$\Phi_{tr} = r_1{}^L Y_{L0}(\hat{\mathbf{r}}_1) \Big[u_{200}(\mathbf{r}_2) \sum_{i=1}^{N} a_i e^{-\alpha_i r_1}$$

$$+ \sum_{\lambda=0}^{2} \sum_{j\lambda=1}^{N\lambda} b_{j\lambda} P_\lambda(\cos\theta_{12}) r_1{}^\lambda r_2{}^\lambda e^{-\beta_{j\lambda}r_1 - \gamma_{j\lambda}r_2} \Big]$$

$$\pm (\mathbf{r}_1 \rightleftarrows \mathbf{r}_2). \tag{34}$$

The $2s$ hydrogenic function was included explicitly, as it is one of the lowest hydrogenic states contained in the trial function and hence likely to make an important contribution to the energy. We can get explicit $2p$ dependence by choosing β_i or $\gamma_i = 0.5$ for one of the terms in the sum multiplying $P_1(\cos\theta_{12})$. Since the energies are degenerate with respect to all possible M values, we have taken $M = 0$. Of the general functions $F(r_1, r_2, r_{12})$ and $G(r_1, r_2, r_{12})$, which may each be expanded as

$$\sum_{\lambda=0}^{\infty} g_\lambda(r_1, r_2) P_\lambda(\cos\theta_{12}),$$

we are retaining only terms through $\lambda = 2$. The omission of all higher λ's leads to the converging of our energies to values somewhat higher than the exact eigenvalues.

As mentioned earlier, the choice of

$$n(= N + N_0 + N_1 + N_2)$$

terms in the trial function leads to an $n \times n$ Hamil-

tonian matrix which, when diagonalized, gives upper bounds to the n lowest eigenvalues of H_{QQ}. More explicitly, we solve the secular equation, $\mathrm{Det}(\mathfrak{IC} - \mathscr{E}\mathfrak{N}) = 0$, where the matrix elements of $\mathfrak{IC}$ and $\mathfrak{N}$ are the coefficients of $c_i c_j$ in the expression $\langle Q\Phi_{ti} | H | Q\Phi_{tr} \rangle$ and $\langle Q\Phi_{tr} | Q\Phi_{tr} \rangle$, respectively. By varying the nonlinear parameters α_i, β_i, and γ_i separately for each of the eigenvalues, we get the lowest possible upper bound for each eigenvalue.

The two-electron Hamiltonian may be written in scaled form as

$$H = -\nabla_1{}^2 - \nabla_2{}^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{2}{Zr_{12}}, \tag{35}$$

where lengths are in units of a_0/Z and Z is nuclear charge of the two-electron system. The corresponding eigenvalues will be the total energy in units of Z^2 Ry relative to the energy of two free electrons at infinity with zero kinetic energy. The spectrum of QHQ will consist of discrete bound states with $\mathscr{E}_s < -0.25$ (units of Z^2 Ry), corresponding to the binding of the second electron to a hydrogen-like atom in the $n = 2$ state, and a continuum with $\mathscr{E} \geq -0.25$. Thus, any eigenvalues that arise from the variational procedure which are ≥ -0.25 have no significance and will converge to -0.25 by taking more terms in the trial function.

If we interpret these states of the compound system as doubly excited states in a central field description ($2s2p$, $2s3p$, etc.), then it is reasonable to expect that the number of such bound states will be infinite for $Z \geq 2$, since the effective asymptotic nuclear charge is $Z - 1$, and there will be an infinite number of Coulomb levels. For $Z = 1$, it seems that the number of compound atom states will also be infinite, as observed by Gailitis and Damburg,[11] owing in this case to the strong electric dipole interaction between the asymptotic electron and the degenerate $n = 2$ levels of hydrogen.

Our results for the lowest discrete eigenvalues of each symmetry obtained with the use of a 9-, 15-, 20-, and 25-term function are given in Table I. A complete simultaneous variation of all the exponential parameters would be prohibitive, so our results represent the lowest eigenvalues obtained by varying some of the parameters and randomly choosing the remaining ones. The states calculated are $^{1,3}S^e$ and $^{1,3}P^o$ for $Z = 1$ and 2. The choice of parities $(-1)^L$ was dictated by the fact that they are the only states which can arise in the scattering by a ground-state hydrogenic system. The state $2p^2\ {}^3P^e$, whose energy also lies in the range of the single continuum, has been shown to exist for H^- and He,[12] but it will not autoionize (no parity change allowed) nor give rise to any resonances in elastic scattering ($^{1,3}P^o$ state).

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[12] E. Wold, Institute for Theoretical Physics, Oslo, Report No. 13, 1962 (unpublished); E. Holøien, Physica Norwegica 1, 53 (1961).

TABLE I. Variational estimates of the lowest eigenvalues of the operator H_{QQ} (compound levels) in units of Z^2 Ry.

System and state	Dimensions of Hamiltonian matrix			
	9×9	15×15	20×20	25×25
H⁻				
$^1S^e(1)$	−0.29728	−0.29737	−0.29741	−0.29744
$^1S^e(2)$	−0.25148	−0.25149	−0.25155	−0.25192
$^3S^e(1)$	−0.25401	−0.25401	−0.25401	−0.25401
$^3S^e(2)$	−0.25012	−0.25013	−0.25013	−0.25013
$^1P^o(1)$	−0.25176	−0.25191	−0.25191	−0.25193
$^1P^o(2)$	−0.25002	−0.25002	−0.25003	−0.25003
$^3P^o(1)$	−0.28331	−0.28457	−0.28500	−0.28504
$^3P^o(2)$	−0.25038	−0.25039	−0.25041	−0.25042
He				
$^1S^e(1)$	−0.38904	−0.38909	−0.38909	−0.38912
$^1S^e(2)$	−0.30906	−0.30926	−0.30926	−0.30956
$^1S^e(3)$	−0.29298	−0.29355	−0.29477	−0.29490
$^1S^e(4)$	−0.26963	−0.27127	−0.27466	−0.27503
$^1S^e(5)$	−0.26784	−0.26928	−0.26997	−0.27000
$^3S^e(1)$	−0.30100	−0.30111	−0.30120	−0.30120
$^3S^e(2)$	−0.27938	−0.27993	−0.28021	−0.28021
$^3S^e(3)$	−0.27249	−0.27547	−0.27672	−0.27672
$^3S^e(4)$	−0.26474	−0.26477	−0.26546	−0.26546
$^3S^e(5)$	−0.26127	−0.26223	−0.26329	−0.26334
$^1P^o(1)$	−0.34427	−0.34511	−0.34554	−0.34579
$^1P^o(2)$	−0.29473	−0.29578	−0.29587	−0.29750
$^1P^o(3)$	−0.27429	−0.27608	−0.27707	−0.27797
$^1P^o(4)$	−0.26938	−0.27048	−0.27136	−0.27205
$^1P^o(5)$	−0.26538	−0.26709	−0.26722	−0.26784
$^3P^o(1)$	−0.37943	−0.37983	−0.38010	−0.38044
$^3P^o(2)$	−0.29032	−0.29103	−0.29123	−0.29141
$^3P^o(3)$	−0.27525	−0.27556	−0.27608	−0.27697
$^3P^o(4)$	−0.26881	−0.26892	−0.26921	−0.26975
$^3P^o(5)$	−0.26359	−0.26389	−0.26393	−0.26656

In H⁻ we found only two eigenvalues for each symmetry lying below the $n=2$ threshold. This is consistent with the expected uncertainties, which are discussed below. In He we limited our attention to the five lowest-lying eigenvalues only. The compound levels are plotted in the form of an energy-level diagram in Figs. 1 and 2.

As a check on our numerical procedures, we have used Φ_{tr} (not ϕ_{tr}) as a trial function for a variational calculation of the lowest-lying bound states of the true Hamiltonian. These results are given in Table II, together with best available values for comparison. Note that our results do converge to the somewhat higher energies; this we might expect because of the omission of $\lambda>2$
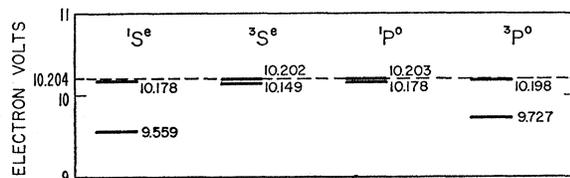
FIG. 1. Energy level diagram of the calculated compound levels below the $n=2$ threshold in H. The energies are in electron volts and represent the excitation energy from the ground state of H (plus free electron of zero kinetic energy).
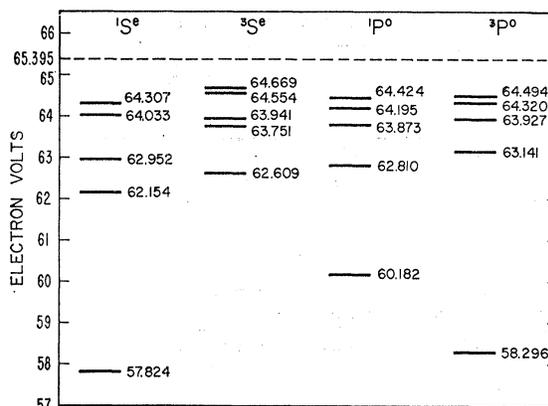
FIG. 2. Energy level diagram of the calculated compound levels below the $n=2$ threshold in He⁺. The energies are in electron volts and represent the excitation energy from the ground state of He.

terms in our trial function. The relatively poor convergence of this type of expansion for the normal states as compared with a trial function containing r_{12} explicitly is well known. However, the inclusion of r_{12} will lead to additional mathematical difficulties in obtaining $Q\Phi_{tr}$. If we take the normal-state results as an indication of the accuracy of our compound-state energies, then we would expect our results to be too high by at most 0.05 eV for H⁻ and 0.1 eV for He. At any rate, these energies represent upper bounds to the exact compound level energies.

TABLE II. Lowest eigenvalues of the operator H (normal levels) in units of Z^2 Ry.

System and state	Present calculation	"Exact" result
H⁻ ^1S	−1.05278	−1.05550[a]
He ^1S	−1.44934	−1.45186[a]
^1P	−1.05994	−1.06192[b]

[a] C. Pekeris, Phys. Rev. 115, 1216 (1959).
[b] C. Pekeris, B. Schiff, and H. Lifsen, Phys. Rev. 126, 1057 (1962).

IV. COMPARISON WITH EXPERIMENT AND OTHER CALCULATIONS

A. Absorption of Continuous Ultraviolet Radiation by He

Experimental results of this kind have been obtained by Madden and Codling[6] by using a continuous source of ultraviolet radiation in the region 160–210 Å. They have resolved about 25 resonances due to compound $^1P^o$ states which lie below the $n=2$, 3, and 4 levels of He⁺. Of the 12 resonances they observe below the $n=2$ state of He⁺, we use the 5 lowest-lying ones for comparison with our calculated eigenvalues.

The observed continuous absorption spectrum shows anomalies which closely obey the Fano form (29). Depending on the value of the parameter q, $(q+\epsilon)^2/$

TABLE III. Excitation energies of lowest lying $^1P^o$ compound states in He as observed in continuous absorption.

λ_{max} (in Å)	Orbital classification	Experimental $\mathscr{E}_s + \Delta_s$ (in eV)	$\mathscr{E}_s$ of Table I (in eV)
206.21 ($\pm$0.05)	$(2s, 2p)$	60.129	60.182
197.56 ($\pm$0.03)	$(sp, 23-)$	62.76	62.810
194.78 ($\pm$0.02)	$(sp, 23+)$	63.65	63.873
193.30 ($\pm$0.05)	$(sp, 24-)$	64.14	64.195
192.33 ($\pm$0.02)	$(sp, 24+)$	64.46	64.424[a]

[a] Dr. Burke (private communication) suggests that this compound level is the lowest lying in the $2pnd$ series, which is expected to lie between the $(sp, 24\mp)$ levels and is too weak to be observed in ultraviolet absorption.

$(1+\epsilon^2)$ has the shape given in Fig. 3. The experimental wavelengths given in Table III correspond to the point for *maximum* absorption. The quantity $(q+\epsilon)^2/(1+\epsilon^2)$ is the ratio of total absorption to background absorption in the vicinity of a resonance. As the background absorption is slowly varying, it may be regarded as constant over the resonance, and $(q+\epsilon)^2/(1+\epsilon^2)$ may be taken as the actual form of the total absorption coefficient.

The displacement of the value of ϵ for maximum absorption from $\epsilon=0$ can be simply found to be $1/q$. Thus, if we define $\mathscr{E}_s+\Delta_s$ as the line center, we find, by setting $\epsilon(E_{max})=1/q$ and using Eqs. (30) and (22),

$$\mathscr{E}_s+\Delta_s=E_{max}-(\Gamma_s/2q),\qquad(36)$$

and this may be evaluated from the experimentally determined E_{max} and line-shape parameters q and Γ_s. A detailed determination of Γ_s and q has been done only for the lowest-lying level,[6] for which

$$q=-2.75,$$

$$\Gamma=0.037 \text{ eV}.$$

Putting these into (36) gives, for the lowest state,

$$(\mathscr{E}_s+\Delta_s)_{exptl.}=60.122 \text{ eV}+0.0067 \text{ eV}=60.129 \text{ eV}.$$

Since the magnitude of the correction for the lowest line (0.0067 eV) is so small and the widths decrease sharply for higher lines, the experimentally deduced values for $\mathscr{E}_s+\Delta_s$ have the values given in the third
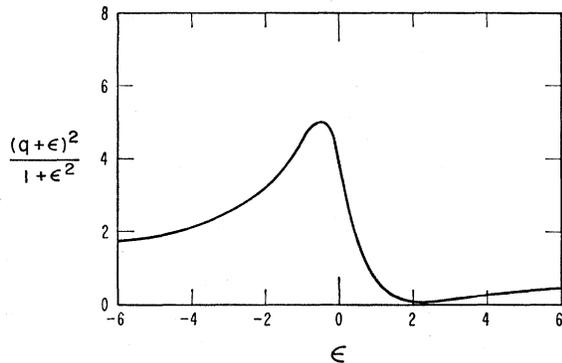
FIG. 3. Fano line shape for $q=-2$.

column of Table III. We list our compound atom $^1P^o$ energy levels from Table I in the fourth column of Table III, where they appear as energy above the ground state of He.

As the uncertainties in our calculated values of $\mathscr{E}_s$ are about -0.1 eV, we cannot reliably deduce the shifts Δ_s by comparison with the experimental values. A purely theoretical evaluation of Δ_s should be possible by means of (20), but this has not yet been done.

It should be mentioned that the $\pm$ sign in the Cooper, Fano, Prats[13] classification of these states (second column, Table III) does not appear explicitly in our variational approach. It originates in their application of perturbation theory, starting with central field nl orbitals as the zero-order approximation, and should not be confused with the $\pm$ signs we use in our trial forms for the singlet and triplet states. In other words, the Cooper, Fano, Prats $\pm$ designation does not describe a basic symmetry of the compound-state wave function but is convenient for the classification of these states.

The quasi-forbidden nature of transitions to the minus states was pointed out by Cooper, Fano, and Prats and verified experimentally. The observed absorption strengths for these states is below that for the plus states by a factor of 1/50 or less. We hope to verify this by computing the transition probabilities with our variational wave functions in the future.

B. Electron Energy Loss Measurement

The energy loss spectrum of the scattered electrons in ionizing collisions with He atoms also gives evidence of He resonance states. In Table IV, we list the results

TABLE IV. Excitation energies of compound states in He as determined by electron energy loss measurements (all energies in eV).

Experimental position of resonance ($\mathscr{E}_s + \Delta_s$)	Closest-lying calculated compound levels
57.9	$57.824[^1S^e(1)]$
58.5	$58.296[^3P^o(1)]$
60.0	not evaluated—believed to be $^1D^e(1)$
60.1	$60.182[^1P^o(1)]$
63.6	$63.751[^3S^e(2)]; 63.873[^1P^o(3)]$
64.5	$64.554[^3S^e(4)]; 64.494[^3P^o(5)]; 64.424[^1P^o(5)]$
64.8	$64.669[^3S^e(5)]$

of Simpson, Mielczarek, and Cooper[5] along with the closest lying $\mathscr{E}_s$'s from Table I. It appears that some of the observed energy-loss resonances could very well be the resultant of a number of closely lying compound states.

The earlier detection by Silverman and Lassettre[3] of two energy-loss peaks in helium at 60.0±0.1 and 63.5

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

± 0.2 eV which have been classified by Fano as $(2s2p)^1P$ and $(sp,23+)^1P$, are fairly consistent with our eigenvalues for $^1P^o(1)$ and $^1P^o(3)$. On the basis of our present results, the higher-energy resonance seen here could be partly due to the $^3S^e(2)$ compound state at 63.751 eV.

It should be noted finally that the results of the present calculation (Table I) predict a number of additional levels in all S and P symmetry states which should, in principle, be observable in such experiments.

C. Elastic Scattering Calculations

Close coupling calculations on the elastic scattering of electrons by H and He$^+$ have been done by Burke and Schey[1] and Burke, McVicar, and Smith.[2] They have found the presence of very narrow resonances at incident energies just below the $n=2$ inelastic threshold, which are interpreted as arising from the presence of compound states. These scattering resonances in H have also been predicted by a number of other workers including Temkin and Pohle,[14] McEachran and Fraser,[15] and Herzenberg and Mandl.[16]

By performing the close-coupling calculation at a very fine mesh of incident energies, they can observe the rapid transit of the scattering phase shift through π radians, as predicted in Eq. (22) for energies in the vicinity of a compound level. This allows the determination of the position of the resonance center $\mathcal{E}_s + \Delta_s$, as well as its width Γ_s.

Their results are summarized in Table V. In the last column we list our lowest lying variational energies in electron volts taken from Table I. For He, the most outstanding discrepancy is in the apparent absence of $^3S^e$ resonances in the scattering results, while we find a normal series of $^3S^e$ compound levels. The statement made by Burke et al.[2] is that no resonances were found having widths greater than 0.001 eV. We did not compute the widths.

There is good agreement for the lowest resonance in each of the series, but it gets poorer for the higher members. It is possible that some of the higher resonances are too narrow for detection in the scattering calculations. It appears that in the $^1P^o$ case there is a good correspondence between the Fano, Cooper, and Prats plus levels [our $^1P^o(1)$, $^1P^o(3)$, $^1P^o(5)$] and the scattering results. This would indicate that the minus levels ($^1P^o(2)$, $^1P^o(4)$) were too narrow to be seen in the scattering calculation. A similar pattern appears with the $^1S^e$ levels, also suggesting that the resonances found in the scattering calculation are $^1S^e(1)$, $^1S^e(3)$, $^1S^e(5)$.

In electron-hydrogen elastic scattering, the two resonances furthest below the inelastic threshold ($^1S^e$, $^3P^o$) are in good agreement with the present variational results. The higher $^1P^o$ resonance is in fair agreement

[14] A. Temkin and R. Pohle, Phys. Rev. Letters 10, 22, 268 (1963).
[15] R. P. McEachran and P. A. Fraser, Proc. Phys. Soc. (London) 82, 1038 (1963).
[16] A. Herzenberg and F. Mandl, Proc. Roy. Soc. (London) A274, 252 (1963).

TABLE V. Results of elastic scattering calculations compared with presently evaluated compound energy levels (all energies in eV and with same reference energies as in Figs. 1 and 2).

System and state		Position of resonance from scattering calculation ($\mathcal{E}_s + \Delta_s$)	Presently calculated $\mathcal{E}_s$
e+H	$^1S^e$	9.6,[a] 9.9[b]	9.559
		10.18[b]	10.178
	$^3S^e$	No resonances found	10.149
			10.202
	$^1P^o$	10.1[a]	10.178
			10.203
	$^3P^o$	9.8[a]	9.727
			10.198
e+He$^+$	$^1S^e$	57.860[c]	57.824
		62.916	62.154
		64.179	62.952
		64.673	64.033
			64.307
	$^3S^e$	No resonances found	62.609
			63.751
			63.941
			64.554
			64.669
	$^1P^o$	60.257	60.182
		63.683	62.810
		64.474	63.873
		64.817	64.195
			64.424
	$^3P^o$	58.352	58.296
		63.132	63.141
		64.247	63.927
		64.701	64.320
			64.494

[a] References 1 and 15; see also P. G. Burke and K. Smith, in *Proceedings of the IIIrd International Conference on the Physics of Electronic and Atomic Collisions*, edited by M. R. C. McDowell (John Wiley & Sons, Inc., New York, 1964), p. 89. Dr. Burke and Dr. Smith have informed us that the very low energy resonances (1.75 and 2.5 eV) reported in the latter reference are not real, but arose from a spurious nonconvergence of the phase-shift calculation.
[b] A. Temkin, p. 107 of above-quoted conference proceedings.
[c] All of these values for e+He$^+$ scattering are taken from the last paper in Ref. 2. Dr. Burke and Dr. Smith have also informed us that in new scattering calculations the ^3S resonances are found as well as additional resonances in the other states, which considerably improve the correspondence with our present results.

but is not located to high accuracy in the scattering calculation.

The presence of at least two resonance levels in every symmetry state is consistent with the infinity of such states pointed out by Gailitis and Damburg.[10] The higher lying compound levels in H$^-$ are predicted to be so close to the continuum that they do not appear bound in our present approximation.

D. Other Variational Calculations

Variational calculations of different types than our present one have been performed on H$^-$ and He by Wu, Hylleraas, Holøien, and Propin. Their results are given in Table VI.

The method used by these investigators is to assume a trial function having primarily the designated configuration (but with the mixing of other configurations) which is a total eigenfunction of L^2, L_z, S^2, and parity. However, they have generally allowed a variable scale parameter to represent an effective nuclear charge. In this way, their trial functions were not of the form $Q\Phi_{tr}$, and hence their results do not represent rigorous

TABLE VI. Other calculated values of the excitation energy of compound levels (all energies in eV and with same reference energies as in Figs. 1 and 2).

System and state		Other results			Present results
H⁻	$(2s^2)^1S$			9.393[a]	9.559[$^1S^e(1)$]
	$(2s2p)^3P$			9.915[b]	9.727[$^3P^o(1)$]
He	$(2s)^1S$	59.354[c]	57.273[a]	57.990[d]	57.824[$^1S^e(1)$]
	$(2p^2)^1S$		62.160[e]	62.757[d]	62.154[$^1S^e(2)$]
	$(2s2p)^1P$			60.375[d]	60.182[$^1P^o(1)$]
	$(2s2p)^3P$	59.805[c]	58.508[b]	59.933[d]	58.296[$^3P^o(1)$]
	$(2p^2)^1D$	60.933[e]		60.190[d]	Not evaluated

[a] E. Holøien, Proc. Phys. Soc. (London) **A71**, 357 (1958).
[b] E. A. Hylleraas, Astrophys. J. **111**, 209 (1950).
[c] T. Y. Wu, Phys. Rev. **66**, 291 (1944).
[d] R. Kh. Propin, Opt. i Spektroskopiya **8**, 300 (1960) [English transl.: Opt. Spectry. (USSR) **8**, 158 (1960)].
[e] E. Holøien, Proc. Phys. Soc. (London) **A72**, 141 (1958).

upper bounds on the desired compound states. This situation was well recognized by these authors. The fact that their trial functions do not have the ground hydrogenic state properly projected out will lead to a lowering of the energy to the energy of a hydrogenic atom in its ground state and a free electron of zero kinetic energy simply by the addition of more terms to the trial function. There will be no convergence to the desired compound-atom eigenvalue.

It should be pointed out that the variational calculation for compound state eigenvalues with rigorous upper bounds can be applied in a practical manner only to two-electron systems. This is because we are required to project out of the arbitrary form of the trial function (Φ_γ) the *exact* ground state wave function for the target atom (with appropriate modifications depending on the identity of particles). In the present calculation, the target atom is hydrogen-like and its ground state is known exactly. However, for the next larger system, a He-like target, we do not have exact ground-state wave functions in simple enough analytic form to allow a variational calculation comparable to the present one. If the ground state is not entirely projected out of the trial function, we do not have the property of rigorous upper bounds. The job of projecting out a two-electron ground-state function of the Hylleraas or Pekeris type would indeed be formidable.

ACKNOWLEDGMENTS

APPENDIX

Given Eq. (25), $P\Psi = \cos\eta_r P\Psi_0 - \sin\eta_r P\Psi_1$, we wish to derive $Q\Psi$, using Eq. (6), and to verify that it is of the same form as Eq. (25), so that the entire wave function Ψ may be written in the form (27). We first

expand the right-hand side of Eq. (6) in the eigenstates Φ_n, as is indicated in Eq. (13), giving

$$Q\Psi = \sum_n \frac{1}{E-\mathcal{E}_n}\Phi_n\rangle\langle\Phi_n QHP\Psi\rangle. \tag{A1}$$

When Eq. (25) for $P\Psi$ is substituted into this and the singular term $n=s$ is written separately, it becomes

$$Q\Psi = \sum_{n\neq s} \frac{\Phi_n\rangle}{E-\mathcal{E}_n}[\cos\eta_r\langle\Phi_n QHP\Psi_0\rangle - \sin\eta_r\langle\Phi_n QHP\Psi_1\rangle]$$

$$+ \frac{\Phi_s\rangle}{E-\mathcal{E}_s}[-\sin\eta_r\langle\Phi_s QHP\Psi_1\rangle + \cos\eta_r\langle\Phi_s QHP\Psi_0\rangle]. \tag{A2}$$

Now, using Eq. (26) for $P\Psi_1$ and remembering (20) and (22), the last term may be written

$$(\hbar^2/2mk)\frac{\Phi_s\rangle\sin\eta_r}{\langle\Psi_0 H_{PQ}\Phi_s\rangle}\left[\frac{\langle\Phi_s H_{QP}GH_{PQ}\Phi_s\rangle + \frac{1}{2}\Gamma_s\cot\eta_r}{E-\mathcal{E}_s}\right]$$

$$= -(\hbar^2/2mk)\frac{\sin\eta_r\Phi_s\rangle}{\langle\Psi_0 H_{PQ}\Phi_s\rangle}.$$

Putting this into the last term in (A2) enables us to write $Q\Psi$ in the form

$$Q\Psi = \cos\eta_r Q\Psi_0 - \sin\eta_r Q\Psi_1, \tag{A3}$$

where

$$Q\Psi_0 = \sum_{n\neq s}\frac{\Phi_n\rangle}{E-\mathcal{E}_n}\langle\Phi_n H_{QP}P\Psi_0\rangle \tag{A4}$$

and

$$Q\Psi_1 = \frac{\hbar^2}{2mk}\frac{\Phi_s\rangle}{\langle\Psi_0 H_{PQ}\Phi_s\rangle} + \sum_{n\neq s}\frac{\Phi_n\rangle}{E-\mathcal{E}_n}\langle\Phi_n H_{QP}P\Psi_1\rangle$$

$$= \frac{(\hbar^2/2mk)}{\langle\Psi_0 H_{PQ}\Phi_s\rangle}\left[\Phi_s\rangle + \sum_{n\neq s}\Phi_n\rangle\frac{\langle\Phi_n H_{QP}GH_{PQ}\Phi_s\rangle}{E-\mathcal{E}_n}\right], \tag{A5}$$

where the explicit expression for $P\Psi_1$ in Eq. (26) has been used. Finally, combining Eqs. (A3) and (25), $\Psi(=P\Psi+Q\Psi)$ may be written

$$\Psi = \cos\eta_r\Psi_0 - \sin\eta_r\Psi_1, \tag{A6}$$

where

$$\Psi_0 = P\Psi_0 + \sum_{n\neq s}\frac{\Phi_n\rangle}{E-\mathcal{E}_n}\langle\Phi_n QHP\Psi_0\rangle \tag{A7}$$

and

$$\Psi_1 = \frac{(\hbar^2/2mk)}{\langle\Psi_0 H_{PQ}\Phi_s\rangle}\left[\Phi_s\rangle + GH_{PQ}\Phi_s\rangle\right.$$

$$\left. + \sum_{n\neq s}\frac{\Phi_n\rangle}{E-\mathcal{E}_n}\langle\Phi_n H_{QP}GH_{PQ}\Phi_s\rangle\right], \tag{A8}$$

where the Green's function G was defined from the left-hand side of Eq. (14). Equation (A6) then is the desired result.