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Improved bound-state method for calculating resonance eigenvectors and properties

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We derive a new criterion for determining an accurate description of the total wave function at the energy of a resonance in the elastic scattering region from a bound-state representation. The criterion is based on an extension of the stabilization and Harris phase-shift methods. We construct the theoretical framework for a bound-state description of the resonance wave function and exhibit its connection to calculations of the bound-state Green's function.

I. INTRODUCTION

The properties of quasibound or resonance states of atomic systems have been the subject of intensive investigation. Resonances have been studied using close-coupling,[1] variational,[2,3] and stabilization methods.[4] Bound-state methods lead to significant simplifications in the calculation of photoionization and scattering processes.[5,6] In this paper we explore a new method for determining an accurate description of the total wave function at an isolated resonance in terms of bound-state configurations in order to obtain a unified description of photoionization and scattering processes in the elastic scattering region. In a preceding paper[5] (hereafter referred to as I) we described the application of bound-state expansions to photoionization of helium and of the negative hydrogen ion.

The total wave function Ψ is associated with a phase shift given by the Breit-Wigner formula

$$\delta = \delta_B + \arctan[\tfrac{1}{2}\Gamma/(E_{\text{res}} - E)], \tag{1}$$

where δ_B is the background scattering phase shift, Γ is the resonance width, and E_{res} is the resonance energy. In this paper, we shall choose a bound-state representation Φ_n with eigenenergy $E_n \approx E_{\text{res}}$ for Ψ by using (1) in conjunction with a previously determined value of δ_B. This choice of Φ_n corresponds to

$$\Phi_n = c_n \Psi(E_n)$$

within some radius R, where c_n is a constant. It enables us to avoid the separate calculation of energy shifts and leads to particularly simple forms for the width and for the dipole transition moments involving the resonance state. We shall present results of calculations on the first ^1S resonance in He to demonstrate the efficacy of this method for resolving uncertainties in the properties of resonances.

II. THEORY

"Core-excited" resonances lie below the ionization threshold and can be described as real bound states of a Hamiltonian projected into a particular subspace of Hilbert space.[7] In a two-electron system, a significant contribution to the function Φ_n comes from a particular doubly excited configuration. However, the energy functional $\langle \Phi_n | H | \Phi_n \rangle / \langle \Phi_n | \Phi_n \rangle$ provides an inadequate guide to the choice of configurations describing background scattering to be included in Φ_n, being generally insensitive to such configurations, whereas the opposite may be true for other matrix elements of the resonance state. We shall derive expressions describing the effect of these background scattering configurations on the width and the dipole transition matrix, using the Fano[8] theory of photoionization as our formal framework.

The discussion shall be limited to the case of an isolated resonance, but it can be easily generalized to the case of overlapping resonances. Following Fano and the development in I, let the total Hamiltonian H have a solution $\Psi(E)$ at energy E, and expand $\Psi(E)$ as

$$\Psi(E) = a_n(\epsilon_n)\phi_n + \int b(E')\psi_{E'}\, dE', \tag{2}$$

where ϕ_n is a real, square-integrable representation of the doubly excited resonance configuration, and the ψ_E represent the background scattering with

$$\langle \phi_n | H | \phi_n \rangle = \epsilon_n ,$$

$$\langle \psi_E | H | \phi_n \rangle = V_{En} ,$$

$$\langle \psi_{E'} | H | \psi_E \rangle = E\delta(E' - E).$$

We can solve for the coefficients a_n and $b(E)$, obtaining

$$\Psi(E) = \frac{\sin\gamma_n}{\pi V_{En}^*}\phi_n - \cos\gamma_n \psi_E + \frac{\sin\gamma_n}{\pi V_{En}^*} \mathrm{P} \int dE' \frac{V_{E'n}\psi_{E'}}{E - E'} , \tag{3a}$$

where

$$\sin\gamma_n \equiv \frac{-\frac{1}{2}\Gamma_n}{\{[E - (\epsilon_n + \Delta_n)]^2 + \frac{1}{4}\Gamma_n^2\}^{1/2}} , \tag{3b}$$

$$\cos\gamma_n \equiv \frac{E - (\epsilon_n + \Delta_n)}{\{[E - (\epsilon_n + \Delta_n)]^2 + \frac{1}{4}\Gamma_n^2\}^{1/2}} , \tag{3c}$$

$$\Gamma_n \equiv 2\pi |V_{En}|^2 \,, \tag{3d}$$

$$\Delta_n \equiv \mathrm{P} \int dE' \, \frac{|V_{E'n}|^2}{E - E'} \,. \tag{3e}$$

The resonance state may be redefined as

$$\phi_n + \mathrm{P} \int dE' \frac{V'_{E'n}}{E - E'} \psi_{E'} \,.$$

Let us examine this state near $E = \epsilon_n + \Delta_n$. We can approximate $\psi_{E'}$ by a real, square-integrable wave function X_j such that $\langle X_j | H | X_{j'} \rangle = \epsilon_j \delta_{jj'}$ and $\langle X_j | \phi_n \rangle = 0$. Then, as in I, we approximate the principal-part integral at $E = \epsilon_n + \Delta_n$ by

$$\mathrm{P} \int dE' \frac{V_{E'n}}{\epsilon_n + \Delta_n - E'} \psi_{E'} \rightarrow \sum_{\epsilon_j \neq \epsilon_n} \frac{\langle \phi_n | H - \epsilon_j | X_j \rangle}{\epsilon_n + \Delta_n - \epsilon_j} X_j \,. \tag{4}$$

The new resonance state, including background configurations, becomes

$$\Phi_n = \phi_n + \sum_{\epsilon_j \neq \epsilon_n} \frac{\langle \phi_n | H - \epsilon_j | X_j \rangle}{\epsilon_n + \Delta_n - \epsilon_j} X_j \,. \tag{5}$$

If Δ_n is small, the summation corresponds to a perturbation correction to ϕ_n owing to mixing with the nondegenerate part of the continuum. The new resonance state, lying approximately at energy

$$E_n = \epsilon_n + \sum_{j \neq n} \frac{|\langle \phi_n | H - \epsilon_j | X_j \rangle|^2}{\epsilon_n - \epsilon_j} \,,$$

corresponds to a resonance at the shifted energy, $E_n = \epsilon_n + \Delta_n$. Φ_n could equally well be obtained by diagonalizing H in the set $\{\phi_n, X_j\}$ to begin with and omitting $\psi_{E'}$. Then Φ_n is one of the eigenfunctions and its eigenenergy E_n automatically includes the energy shift. The principal-part integral, $\mathrm{P} \int dE' \times [V_{En}/(E - E')] \psi_{E'}$, no longer appears in (3a); thus the difficulties associated with principal-part and double-continuum integrals are avoided. Equation (3a) becomes

$$\Psi(E) = [(\sin\gamma_n)/\pi V^*_{En}]\Phi_n - \cos\gamma_n \, \psi_E \,, \tag{6}$$

with the definitions of γ_n and V_{En} having Φ_n in place of ϕ_n. This will not change their values, as we shall show below. The sensitivity of the width and transition moment to the choice of background configurations X_j was discussed in I.

We seek a criterion to determine when we have included a sufficiently complete representation of the background scattering in our basis X_j, and when a particular root of the diagonalization of the Hamiltonian in the basis $\{\phi_n, X_j\}$ lies at the resonance energy. Previous calculations[9,10] have involved elimination of the background scattering configurations from the resonance state entirely and the separate solution of the background scattering problem. In Feshbach notation,[11] this choice corresponds to the projector Q such that

$$Q = 1 - |\phi_0\rangle\langle\phi_0| = 1 - P \,, \tag{7}$$

where ϕ_0 is asymptotically an eigenfunction of the system constructed with one electron in its ground state.

We shall now describe a method of choosing $\Phi_n \cong c_n \Psi(E_{\text{res}})$ such that the background scattering is included in Φ_n. Let Ψ_T be a trial solution with asymptotic form $S(kr + \delta_T)$, where S is a properly symmetrized regular Coulomb (or Bessel function) product wave function describing the scattering of an incoming particle by the core. We shall evaluate the matrix element in a sphere of radius R,

$$\langle \Psi_T | H - E | S(kr + \delta) \rangle_R \,, \tag{8}$$

where R lies beyond the range of the interaction potential. It can be shown that[12]

$$\langle \Psi_T | H - E | S(kr + \delta) \rangle_R = \langle S(kr + \delta) | H - E | \Psi_T \rangle^*_R - \left(\Psi^*_T \frac{dS}{dr} (kr + \delta) - S(kr + \delta) \frac{d\Psi^*_T}{dr} \right)_{r = R} \,, \tag{9}$$

where the last term has been integrated over the core variables. As $r \rightarrow \infty$, $\Psi_T \rightarrow (\pi k)^{-1/2} S(kr + \delta_T)$, and

$$\langle \Psi_T | H - E | S(kr + \delta) \rangle_R = \langle S(kr + \delta) | H - E | \Psi_T \rangle^*_R - \pi^{-1} \sin(\delta_T - \delta). \tag{10}$$

If Ψ_T is chosen to be a single square-integrable function θ, proportional to $\Psi(E)$ for $r < R$, and if we assume Ψ attains its asymptotic form $S(kr + \delta)$ at some distance less than or equal to R, then (10) becomes

$$\langle \theta | H - E | S(kr + \delta) \rangle \cong 0, \tag{11}$$

where we have dropped the subscript R because θ is negligible outside R. Equation (11) is simply the Harris variational expression[13] for the phase shift. Now

$$\delta(E) = \delta_B(E) + \gamma_{\text{res}}(E), \tag{12}$$

where γ_{res} is the resonance phase shift defined in (3) for a bound-state representation. At the resonance energy E_{res}, $\gamma_{\text{res}} = \frac{1}{2}\pi$. Let $C(kr)$ be the irregular Coulomb (or Bessel function) product wave function. Since asymptotically

$$S(kr + \delta_B + \tfrac{1}{2}\pi) = \cos\delta_B [C(kr) - \tan\delta_B S(kr)] \,,$$

we obtain from (11) and (12)

$$\tan\delta_B = \frac{\langle\theta|H - E_{\text{res}}|C(kr)\rangle}{\langle\theta|H - E_{\text{res}}|S(kr)\rangle}. \tag{13}$$

The calculation of δ_B in the neighborhood of the resonance is separable from the calculation of θ itself and may be accomplished by using close coupling,[14] Green's function,[5,15] or other techniques.[3,8,16] As we show in Sec. IV, E_{res}, Γ, and the dipole matrix element are relatively insensitive to δ_B. The ratio in (13) is highly sensitive to the admixture of singly excited configurations in θ. Therefore if $\tan\delta_B$ is already known, Eq. (13) may be used as an extra condition which the function θ must satisfy to be an adequate approximation to the exact scattering solution $\Psi(E)$ at the resonance energy. This is the criterion we have sought.

Equation (13) would be exact if θ were exactly proportional to $\Psi(E_{\text{res}})$ within R and zero beyond R. In general, bound-state functions employed in Harris calculations, and those employed in this work, do not go to zero at R, but have an exponential tail. Some error is thereby introduced, which may be explored by varying the expansion set $\{\phi_n, X_j\}$.

III. RESONANCE WIDTH AND TRANSITION MOMENT

The resonance width has the form

$$\Gamma = 2\pi|\langle\phi_n|H - E|\psi_E\rangle|^2, \tag{14}$$

where ϕ_n and ψ_E are the same as in Eq. (3). ψ_E has the form[12] $\chi + S(kr + \delta_B)$, where χ goes to zero at large r. ψ_E can also be expanded[5] in the set $\{X_j\}$ such that

$$\psi_E = S(kr + \delta_B) + \sum_{\epsilon_j \neq E} \frac{X_j\langle X_j|H - E|S(kr + \delta_B)\rangle}{E - \epsilon_j}. \tag{15}$$

Then the matrix element in Eq. (14) takes the form

$$\langle\phi_n|H - E|\psi_E\rangle = \left\langle \phi_n|H - E| \left(1 + \sum \frac{X_j\langle X_j|(H - E)}{E - \epsilon_j}\right) S(kr + \delta_B)\right\rangle = \left\langle \phi_n + \sum \frac{\langle\phi_n|H - E|X_j\rangle X_j}{E - \epsilon_j} |H - E|S(kr + \delta_B)\right\rangle$$

$$= \langle\Phi_n|H - E|S(kr + \delta_B)\rangle, \quad E \simeq E_{\text{res}}, \tag{16}$$

where, by Eq. (5), $\Phi_n \cong c_n\Psi(E_{\text{res}})$. This transformation also leaves γ_n unchanged (since $E_n = \epsilon_n + \Delta_n$ as well) and avoids the calculation of any principal-part integrals. Therefore if Γ is evaluated using $S(kr + \delta_B)$ on the right-hand side, the proper bound-state function on the left-hand side is Φ_n. Previous authors have not always taken care that the two functions be complementary, and this neglect may lead to serious errors in Γ when δ_B is large. Then $(H - E)|\chi\rangle$ is large, and the proper selection of $\{\phi_n, \psi_E\}$ is crucial.

The normalization constant c_n is derived from (3) by letting $E \to \epsilon_n + \Delta_n$. Then $\cos\gamma_n \to 0$ and

$$\Psi(\epsilon_n + \Delta_n) = \frac{\Phi_n}{\pi\langle\Phi_n|H - E|S(kr + \delta_B)\rangle}. \tag{17}$$

In Eq. (5) we have redefined the resonance state to include a representation of the singly excited configurations of importance which implied $\Phi_n \cong c_n\Psi(E_n)$. Miller[12] assumed $\Phi_n \cong c_n\Psi$ in calculating the resonance width, but had no condition such as Eq. (13) to ensure the validity of this assumption. Hazi and Fels[17] made the same assumption and verified their results with a graphical procedure (cf. Sec. IV).

Bhatia, Burke, and Temkin[9] have attempted to solve this problem by calculating the full background scattering function to be used with a θ which is orthogonal to the ground state of the target. Their approach corresponds to calculating the left-hand side of Eq. (16) using a close-coupling representation for ψ_E, whereas we calculate the last matrix element in Eq. (16). We might equally well have applied the bound-state method to the calculation of the background scattering function instead of Φ_n, as suggested by the second term in Eq. (16). The same remarks apply to the calculation of the dipole transition matrix element.

Finally, by choosing Φ_n proportional to $\Psi(\epsilon_n + \Delta_n)$, we automatically exclude $S(\epsilon_n + \Delta_n)$ from Ψ [since $\cos\gamma_n = 0$ in Eq. (6)] and hence avoid entirely the problem of orthogonalizing S to Φ_n. In addition, we need not project X_j or ϕ_n out of S because the overlap terms make no contribution to $\langle\Phi_n|H - E|S\rangle$.

To see how operators other than the Hamiltonian depend on the choice of ϕ_n and ψ_E, we have explored the behavior of the dipole transition operator

$$\langle\Psi(E)|\vec{\mathrm{D}}|\phi_b\rangle = \left\langle \Psi(E) \middle| \sum_i e\vec{\mathrm{r}}_i \middle| \phi_b \right\rangle,$$

where ϕ_b is some real bound state of the system. In the Fano formalism we have

$$\langle\Psi(E)|\vec{\mathrm{D}}|\phi_b\rangle = \frac{\sin\gamma_n}{\pi V^*_{En}}\langle\phi_n|\vec{\mathrm{D}}|\phi_b\rangle - \cos\gamma_n\langle\psi_E|\vec{\mathrm{D}}|\phi_b\rangle + \frac{\sin\gamma_n}{\pi V^*_{En}} \mathrm{P}\int dE' \frac{\langle\phi_n|H - E|\psi_{E'}\rangle\langle\psi_{E'}|\vec{\mathrm{D}}|\phi_b\rangle}{E - E'}. \tag{18}$$

The terms in the last integral include the contributions of background scattering configurations at $E' \neq E$. If $\phi_b \rightarrow \phi_n$ is a two-electron transition (as in $1s^2 \rightarrow 2s2p$ in helium), these configurations may be very important. Our choice of

$$\Phi_n = \phi_n + \sum_{\epsilon_j \neq E} \frac{X_j \langle X_j | H - E | \phi_n \rangle}{E - \epsilon_j} \approx c_n \Psi(E_{\text{res}})$$

eliminates the calculation of the principal-part integral by including the background scattering in Φ_n. Our expression is simply

$$\langle \Psi(E_{\text{res}}) | \vec{\mathrm{D}} | \phi_b \rangle \cong \frac{\langle \Phi_n | \vec{\mathrm{D}} | \phi_b \rangle}{\pi V^*_{En}} . \tag{19}$$

IV. THE FIRST ^1S RESONANCE IN HELIUM

The first ^1S resonance in helium has been studied extensively using close-coupling,[14] root-stabilization,[18] and projection[9] techniques and the Harris variational method.[13,20] In addition, the total phase shift in the elastic ^1S channel for e-He$^+$ scattering has been studied using many different methods.[14,15,19,21,22] The polarized-orbital phase shift[19] is in excellent agreement with the Harris and close-coupling values well removed from the resonance because the background scattering is dominated by the polarization. Therefore since the polarized-orbital method includes only single excitations, it provides an excellent approximation to the nonresonance phase shift δ_B near the resonance energy.

We have diagonalized the total Hamiltonian in a square-integrable set of the form

$$X_j = (1 \pm \mathrm{P}_{12}) r_1^l r_2^m r_{12}^n e^{-\alpha r_1 - \beta r_2} Y_{LM}(\hat{\vec{\mathrm{r}}}_1, \hat{\vec{\mathrm{r}}}_2) \tag{20}$$

to obtain eigenvectors θ_n, where

$$\theta_n = \sum_j c_j X_j ,$$

such that

$$\langle \theta_m | H - E_n | \theta_n \rangle = 0 \tag{21}$$

for all m, n. The basis sets $\{l, m, n; \alpha, \beta\}$ were chosen in three ways. The first set consisted of all 50 X_j such that $l + m + n \leq N$ where $N = 1-6$ and $\alpha = \beta = 1.1-1.2$. This set is identical to that employed in the Harris calculations of Shimamura[21] and Bhatia.[23] The second set was chosen as the first 50 functions with $l + m + n \leq 7$ but $n \leq 4$ and $\alpha = \beta = 0.9-1.0$. This set corresponded to roughly the same region of stability for the energy as set 1 as shown in Tables I and II. The third set consisted of 47 functions from the second set, the functions $(l, m, n) = (0, 6, 0)$, $(0, 5, 1)$, and $(0, 4, 2)$ having been deleted. These functions have been discussed[18] with regard to the ^1P resonances in helium, and their presence or absence has a strong effect on the resonance energy, as seen in Table II. In the ^1P case, the deletion of these states moves pseudoresonent eigenvalues away from the resonance energy. In the ^1S case, the *addition* of these functions moves the psuedoresonant vectors away. Because of the close proximity of their eigenvalues to the resonance and the diffuse nature of these three functions, they strongly affect the degree of configuration mixing of the *nsnl* function with configurations resembling the 1*skl* background.

The irregular Coulomb function $C(kr)$ was represented by a combination of regular scattering functions[24] $S(kr)$ in order to avoid the singular point at $r = 0$. This procedure differs from other calculations[13,21] which have employed an irregular

TABLE I. Set 1.

Parameters optimized by Eq. (13)

δ_B	α, β	E_n (Ry)	Γ	
			(10^{-3} a.u.)	(eV)
0.300	1.148	−1.556 34	4.60	0.125
0.355	1.158	−1.556 08	4.58	0.125
0.400	1.166	−1.555 87	4.58	0.125

Stabilization method

α, β	E_n	$E_n + \Delta_n$ [a]	$\dfrac{\langle \theta_n \lvert H - E_n \rvert C(kr) \rangle}{\langle \theta_n \lvert H - E_n \rvert S(kr) \rangle}$	Γ_n [b]	
				(10^{-3} a.u.)	(eV)
1.10	−1.557 68	−1.555 96	0.005 64		
1.15	−1.556 29	−1.556 03	0.318	4.575–4.576	0.124
1.20	−1.554 98	−1.556 06	0.679		

[a] Hazi-Fels energy-shift approximation calculated using $\delta = 0.365$ and $\Gamma = 4.575 \times 10^{-3}$ a.u.

[b] See Fig. 3.

TABLE II. Set 2.

Parameters optimized by Eq. (13)

δ_B	α, β	E_n (Ry)	Γ (10^{-3} a.u.)	Γ (eV)	D_{bn}(a.u.)
0.300	0.940	−1.556 27	4.75	0.129	
0.355	0.949	−1.556 01	4.73	0.129	0.2174
0.400	0.956	−1.555 80	4.73	0.129	

Stabilization method

$\alpha, \beta; N$	E_n	$E_n + \Delta_n$	$\frac{\langle\theta_n \vert H-E_n \vert C(kr)\rangle}{\langle\theta_n \vert H-E_n \vert S(kr)\rangle}$	Γ_n [a] (10^{-3} a.u.)	Γ_n [a] (eV)	D_{bn}(a.u.)
0.90; 50	−1.557 53	−1.555 80 [b]	0.006 36			0.2172
0.95; 50	−1.555 98	−1.556 05 [b]	0.377	4.720–4.722	0.128	0.2174
0.99; 50	−1.554 79	−1.555 86 [b]	0.721			0.2182
0.93; 47	−1.545 40	−1.5574 [c]	30.8			
0.95; 47	−1.540 66	−1.5579 [c]	−12.2	5.1–5.5	0.139–0.150	0.2123
0.98; 47	−1.519 92	−1.5559 [c]	−4.1			

[a] See Figs. 4 and 5.

[b] Using $\delta = 0.379$, $\Gamma = 4.72 \times 10^{-3}$ a.u. in the Hazi-Fels approximation.

[c] Using $\delta = 0.39$, $\Gamma = 5.5 \times 10^{-3}$ a.u. in the Hazi-Fels approximation.

function multiplied by an arbitrary cutoff term.

Figures 1 and 2 show the values of E_n and $\langle \theta_n | H - E_n | C(kr)\rangle / \langle \theta_n | H - E_n | S(kr)\rangle$ for the first two sets. Choosing $\delta_B = 0.355$ ($\tan\delta_B = 0.371$), the polarized-orbital value, we obtain $E_{\text{res}} = 1.556\,08$ and $E_{\text{res}} = 1.556\,01$ Ry from sets 1 and 2, respectively. The corresponding values of the width are 0.125 and 0.129 eV, respectively. Since the two sets differ by configurations for which $l + m + n = 7$, some of which are very diffuse, and since they have very different ranges as determined by α and β, the exponential tails occur at considerably different values of r and will make different contri-

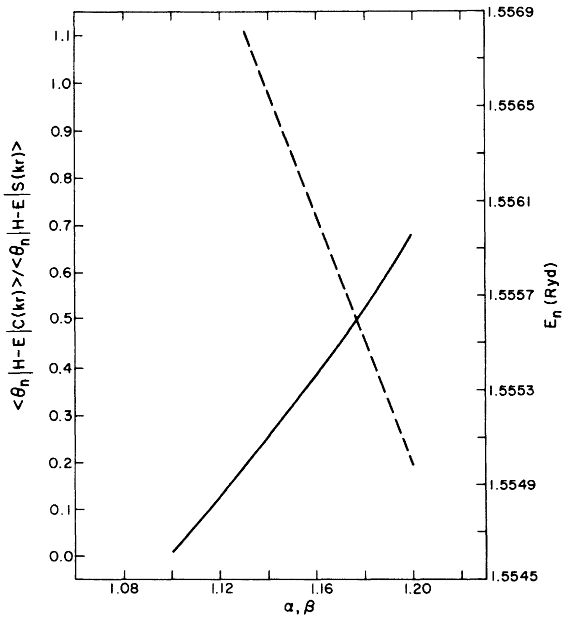

FIG. 1. Matrix-element ratio in Eq. (13) (solid curve) and the energy (dashed curve) as a function of the nonlinear parameters in the basis set for set 1.

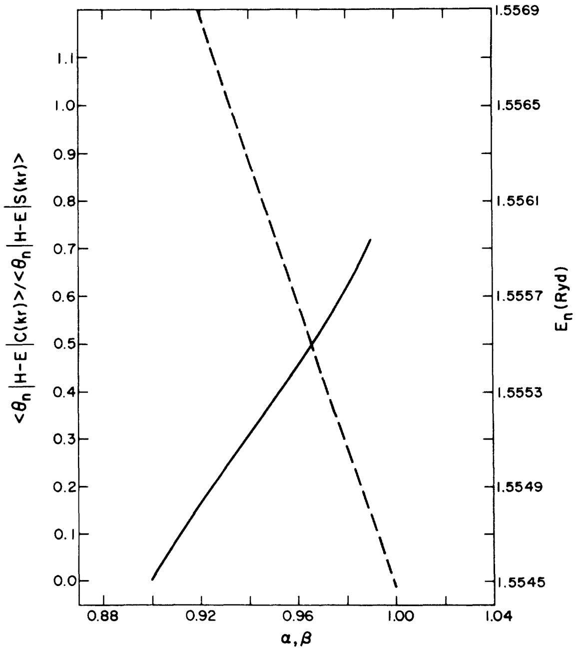

FIG. 2. Same as Fig. 1 but for set 2.

butions to the integrals over S and C. Hence the discrepancies in E_{res} and Γ are a measure of the uncertainty introduced by the tail. This discrepancy may also indicate the extent to which θ_n has failed to achieve the asymptotic form $S(kr+\delta_B+\frac{1}{2}\pi)$. For $\delta_B=0.355$, the matrix elements differ by about 1.5% for the two sets, leading to similar agreement between the widths and the determination of E_{res} to four decimal places. To indicate the insensitivity of the results over a range of δ_B, we have listed in Tables I and II results derived assuming $\delta_B=0.3$ and 0.4, although the real uncertainty in δ_B is much smaller.

The value of the method in selecting a basis set for representing the resonance is seen in Table II from the results for the 47-function set. Nowhere are the values of $\langle\theta_n|H-E_n|C(kr)\rangle/\langle\theta_n|H-E_n|S(kr)\rangle$ near the polarized-orbital value of δ_B. In fact, $\langle\theta_n|H-E_n|S\rangle$ vanishes near $\alpha=\beta=0.94$. This means that these vectors are a poor representation of $\Psi(E_{\text{res}})$, at least for the values of α and β studied here. This basis set probably provides an incorrect representation of background scattering configurations in the resonance vector, and is inadequate as a representation of $\Psi(E)$ at E_{res}.

We have also calculated dipole transition matrix elements D_{bn} for the transition

$$1s2p\,{}^1P\rightarrow(2s^2)\,{}^1S$$

for sets 2 and 3. This transition is basically a one-electron transition because of the admixture of the $2p^2$ configuration in the ${}^1S$ state. However, the effect of dropping the three diffuse configurations still amounts to several percent of the total matrix element, much greater than the variation found for the 50-function set over the range of δ. We expect an even larger effect in cases where the resonance transition is basically two-electron, as for the case

$$(1s^2)\,{}^1S\rightarrow 2s2p\,{}^1P$$

in helium. We shall discuss this case below.

We wish to emphasize that stability, especially with regard to variations in nonlinear parameters, appears to be a less precise criterion for determining a good representation of $\Psi(E_{\text{res}})$ than our criterion, Eq. (13), as the 47-function set demonstrates. Not only will error in the representation of background scattering lead to incorrect calculations of δ, the total phase shift, but other properties calculated from this representation, such as $\Gamma_n(E)$ or D_{bn}, will be incorrect.

Let us compare our method for choosing resonance vectors with the Harris and stabilization methods. The Harris method for isolated resonances allows direct determination of δ from an eigenvector θ_n by

$$\begin{aligned}\delta(E)&=\delta_B(E)+\arctan\gamma_n\\&=\delta_B(E)+\arctan\left(\frac{\frac{1}{2}\Gamma_n}{E_{\text{res}}-E}\right)\\&=-\arctan\left(\frac{\langle\phi_n|H-E_n|S\rangle}{\langle\phi_n|H-E_n|C\rangle}\right).\end{aligned}\tag{22}$$

As the nonlinear parameters are varied, if $\theta_n\rightarrow\Phi_{\text{res}}$, then $\delta(E)\rightarrow\delta_B(E_{\text{res}})+\frac{1}{2}\pi$. However, since δ_B is an unknown, a unique set $(\delta_B, E_n, \Gamma_n)$ is difficult to determine with high accuracy. Equation (22) is equivalent to the condition (13). Our method corresponds to using the Harris method in reverse. Given δ_B from another source, we use Eq. (13) to select Φ_n from among many θ_n, and, in particular, from among the θ_n with E_n near E_{res}. Thus within the uncertainties in our calculation, basis sets 1 and 2 generate equally good representations of $\Psi(E)$ for $E\approx E_{\text{res}}$ and Eq. (13) helps us to determine more precisely both E_{res} and the function $\Phi_n\alpha\Psi(E_{\text{res}})$. In contrast, set 3 does not satisfy Eq. (13) for any reasonable guess for δ_B using the range of α and β tested here, and will be rejected altogether.

The stabilization method has been used to calculate E_{res} and Γ_{res} by a technique suggested by Hazi and Fels.[17] They assume that

$$\theta_n\cong c_n\Psi(E_{\text{res}})\tag{23}$$

for any θ_n with $E_n\sim E_{\text{res}}$, and show that Γ_{res} is independent of θ_n even if E_n is not exactly equal to E_{res}, providing that the correct background phase shift is used in calculating Γ. The widths Γ and δ_B are simultaneously determined by calculating Γ for several θ_n with $E\sim E_{\text{res}}$. The fact that $\Gamma_{\text{res}}\neq\Gamma(E_n)$ if some other phase shift is used leads to a simple formula for E_n-E_{res} which gives an improved determination of the resonance position. However, the basic assumption (23) is valid only for $E_{\text{res}}-E_n\ll\Gamma_{\text{res}}$ and for θ_n including an adequate number of singly excited configurations in it. Hazi and Fels calculate Γ from the matrix element

$$\langle\theta_n|H-E_n|S(kr+\delta_B)\rangle,$$

which they claim is equal to $\langle\theta_n|H-E_n|\psi_{E_n}\rangle$. For any θ_n and $\{\psi_E\}$ satisfying (2) and (3), even when (23) is not satisfied, we have

$$\langle\Psi(E_n)|H-E_n|\psi_{E_n}\rangle\alpha\left\langle\theta_n+\mathrm{P}\int\frac{V_{E'n}}{E_n-E'}\psi_{E'}\,dE'-\pi V^*_{E_n}\cot\gamma_n\,\psi_{E_n}\middle|H-E_n\middle|\psi_{E_n}\right\rangle=\langle\theta_n|H-E_n|\psi_{E_n}\rangle\tag{24}$$

from Eq. (3) and the condition $\langle\psi_{E'}|H-E|\psi_E\rangle=0$. However, it is not possible to replace ψ_{E_n} in the last term of Eq. (24) by its asymptotic form $S(kr+\delta_B)$ since $(H-E_n)\theta_n\neq 0$ in the interior region. On the other hand, in the middle matrix element of Eq. (24) $|\psi_{\rm res}\rangle$ may be replaced by its asymptotic form, but then the parts involving $\psi_{E'}$ and ψ_{E_n} no longer vanish; thus this term is not equal to $\langle\theta_n|H-E_n|S\rangle$.

For a small background phase shift these extra terms should be small. But when δ_B is not small they must be calculated. Furthermore, even if θ_n included an adequate number of singly excited configurations in it, so that the principal-part integral could be omitted, the condition $E_n-E_{\rm res}\ll\Gamma_{\rm res}$ must be satisfied to justify dropping the $\langle\cot\gamma_n\psi_{E_n}|H-E_n|S\rangle$ term. Hazi and Fels[17] avoid the latter problem by using stabilized θ_n only. We suggest, however, that whatever the size N of the basis set used in determining θ_n, more accurate results may be obtained by simply using Φ_n for which Eq. (23) is valid at $E=E_{\rm res}$, so that

$$\langle\Phi_n|H-E_{\rm res}|\psi_{E_n}\rangle=\langle\Phi_n|H-E_{\rm res}|S(kr+\delta_B)\rangle,$$

where the Φ_n satisfies Eq. (13) for the known δ_B. This criterion is more precise then stability and has an uncertainty directly related to the uncertainty in δ_B. However, our method depends upon having a prior knowledge of δ_B.

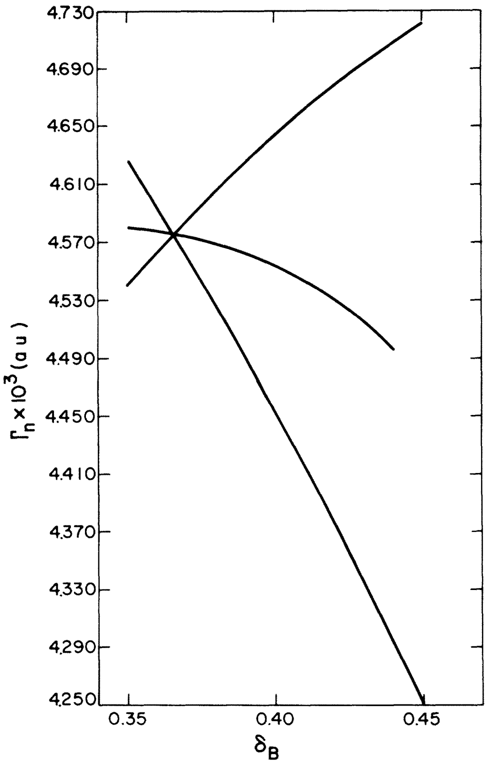

FIG. 3. Calculation of the width by the method of Hazi and Fels (Ref. 17) for the three θ_n of set 1 (cf. Table I).

We illustrate this point in Figs. 3–5. We determined δ_B and Γ_n by the method of Hazi and Fels for the 50- and 47-function sets, respectively. Bhatia[23] previously obtained $\delta_B=0.40$ from this method, but our values of $\delta_B=0.365$ and $\delta_B=0.379$ from the 50-function sets are closer to the polarized-orbital value.

Results of our method and the Hazi-Fels method may be compared in Tables I and II. The Hazi-Fels approach works remarkably well for the 50-function sets. The resonance position, including the Hazi-Fels approximation to the energy shift Δ_n, is in excellent agreement with our value calculated for $\delta_B=0.355$ which corresponds to $\Delta_n=0$. However, for the 47-function basis set, the Hazi-Fels method leads to a value of Γ with a rather large uncertainty and an unsatisfactory values of E_n which cannot be corrected consistently by the energy shift even though the uncertainty in the derived δ_B is not large. The discrepancy arises from the fact that $E_n-E_{\rm res}>\Gamma$ for these vectors, so that the contribution of terms containing $\psi_{E'}$ cannot be ignored; that is, these sets yield poor representations of $\Phi(E_n)$. In fact, the results would be even

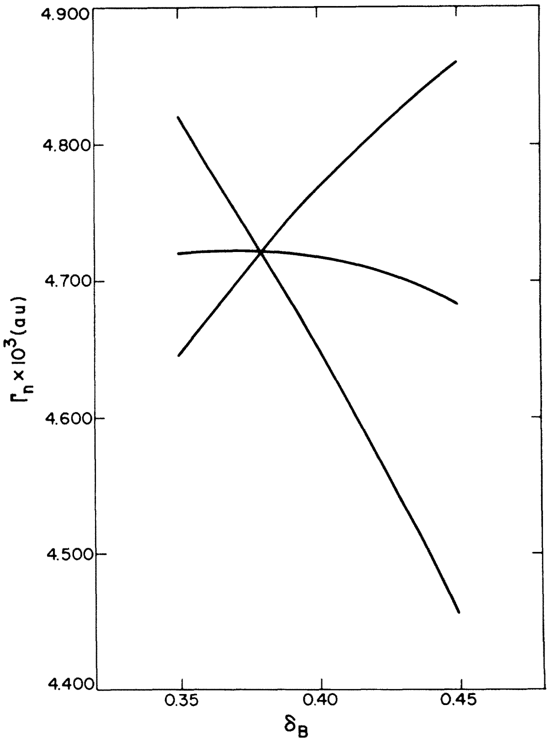

FIG. 4. Same as Fig. 3 but for set 2 (cf. Table II).

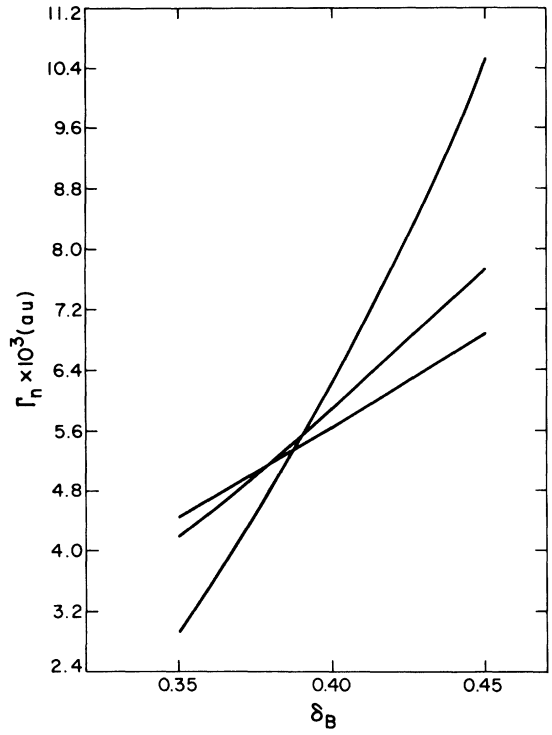

FIG. 5. Same as Fig. 3 but for set 3 (cf. Table II).

worse, but the bulk of δ_B, about 85%, comes from the static-exchange term involving $S(kr)$ only and the contribution of the configurations X_j to Γ is not large.

This example demonstrates several points. First, the properties of a resonance may be extremely sensitive to changes in a few of the functions in the basis set which represent single excitations, even though the energy is not. Hence considerable care is necessary when such small changes are made. Second, while it may be argued that the θ_n from the 47-function set are not well stabilized, the stabilization criterion is apparently not as sensitive as our phase-shift criterion to the admixture of single excitations. Third, the Hazi-Fels method may lead to inaccurate values of the resonance width and energy if improperly applied with the unshifted eigenenergy not lying well within one resonance width of the true energy. However, this method does generate a self-consistency criterion, as illustrated by the triangular crossing of curves in Fig. 5. Our criterion, Eq. (13), selects more precisely the best θ_n limited only by the uncertainty in δ_B.

Optimization of the nonlinear parameters α and β for the 47-function set by our method leads to new values of $\alpha=\beta=0.725$. This gives $E_{\text{res}}=-1.556\,13$ Ry, which is in excellent agreeement with the resonance positions from the two 50-function basis sets.

Having recognized all of the abovementioned difficulties, we conclude that the Hazi-Fels method may be very useful (i) when δ_B is not large *and* the basis set has no complications such as the configuration interaction involved in the 47-function set and (ii) when δ_B is not otherwise available.

V. THE FIRST ^1P RESONANCE IN HELIUM

A related problem arises in the calculation of the transition matrix element $\langle 1s^2\,{}^1S|D|2s2p\,{}^1p\rangle$ where theory[5,9] and experiment[25] are about 50% apart. Here δ_B is very small, but because we are dealing with a two-electron transition, the contribution of singly excited X_j to the $2s2p\,{}^1p$ function is critical. To calculate the resonance oscillator strength the matrix element $\langle 1s^2|D|\Psi(E_{\text{res}})\rangle$ is required, and a good approximation to $\Psi(E_{\text{res}})$ must include an adequate representation of the background configurations. We suspect that the discrepancies can be traced to the use of an improper basis set as a result of complications arising from the three aforementioned "diffuse" configurations. In this case, the static-exchange phase shift is rather poor, and background correction terms to any inexact representation θ_n will be both important and difficult to calculate. The stabilization calculations of Bhatia[23] lead to a value $\delta_B=0.015$ in the ^1P case. A well-converged value of $\delta_B=-0.00670$ has been calculated recently using a Green's-function method,[15] indicating that the resonance representation of Bhatia is inadequate. Bhatia, Burke, and Temkin[9] have calculated a background scattering function using the close-coupling method which is employed with a projected representation of Φ_n. This potential scattering function gives $\delta_B=-0.025$, also in substantial disagreement with the Green's-function calculation. We suspect neither representation leads to an accurate representation of $\Psi(E_{\text{res}})$. Our method should be more accurate because scattering information is available from two sources: the energy operator, ensuring a good representation for the doubly excited configuration in Ψ, and the background scattering phase shift, leading to a good representation of the singly excited configurations in Ψ.

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