

Multichannel configuration-interaction theory: Application to some resonances in helium*

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Using the method of configuration interaction as applied to autoionization by Fano, expressions involving the reaction matrix K in the basis of the original configurations are given for the width and resonance energy. The expression obtained for the width is a Fermi "golden rule" type formula similar to that proposed by Miller. The expression for the resonance energy changes only slightly as the independent energy parameter varies, and therefore it is possible to consider a particular resonance among closely spaced resonances without elaborate search procedures. Application is made to the $(nl^2)^1S$ autoionizing states of He below the $n=4$ threshold. No significant near-neighbor resonance interactions were found despite the small energy intervals between adjacent levels. The results indicate the $5s^2$ state falls below the $n=4$ threshold, which is reflected in the small width given by our results. Widths, resonance energies, relative decay probabilities for each of the open channels, and Fano-Cooper cross-section parameters are given for all the states considered. Comparison is made with experiment and other theories where possible.

I. INTRODUCTION

Fano's configuration-interaction (CI) theory for autoionizing states¹ has provided the basis for much of the experimental work and has supplied many useful relationships between the various theoretical approaches to resonances. Fano assumed a basis set of bound and continuum subsets which diagonalize the Hamiltonian within but not between subsets. He then provided a prescription, not unlike the CI theory for bound states, for constructing the formal solution of the Schrödinger equation in this basis. He obtains formulas for the shape of the resonance curve in terms of a phenomenological shape parameter q , the resonance energy E^r , and width Γ of the autoionizing state. These formulas give the shape of the spectral line for a radiative transition from the ground state,¹ and the shape of the electron elastic scattering cross section near a resonance.^{2,3} As such they provide the basis for the interpretation of photon absorption and elastic scattering experiments.⁴

In providing relationships to other theories, Fano originally compared his CI theory to the resonance theory of Breit and Wigner.⁵ Subsequently Fano and Prats⁶ linked the CI theory with the Lippmann-Schwinger scattering theory⁷ and more recently Ressayre and Lefebvre⁸ related Fano's CI approach to the Green's-function method. Miller's technique⁹ is related to Fano's

work by the present authors (Sec. II B). Its relationship to the Kohn variational principle when applied to the Feshbach equations,¹⁰ to the well-known close-coupling theory,⁴ and to the quantum theory of decaying states¹¹ is also apparent. Finally the several quasivariational techniques⁴ may be regarded as methods for obtaining bound-state functions which may be subsequently used in a CI calculation.¹²

Despite the central role of the CI theory in developing our understanding of resonances, it has not been widely utilized as a computational technique. The single direct application known to the authors is limited to one channel.¹³ The barrier to wider applications of Fano's theory is the requirement for prediagonalization; i.e., one must have sets of bound and continuum functions which diagonalize the Hamiltonian within their respective subspaces. Fano and Prats⁶ give a technique for diagonalizing in the continuum subspace. However, to our knowledge they have never presented expressions for E^r and Γ in terms of the original matrix elements for the general N bound states and M continua case. Altick and Moore^{13,14} accomplished the diagonalization numerically.

In the present work we complete and extend some of the ideas mentioned above and apply the CI method to some resonances in He. In Sec. II we review the generalized CI formalism which, following Prats and Fano,¹⁵ avoids the

prediagonalization procedure. We generalize their work by deriving final expressions for the resonance energy E^r and width Γ which involve only the matrix elements of the original basis set for N bound states and M continua. Like Fano and Prats⁶ we relate the present approach to the Lippmann-Schwinger scattering theory, thus permitting the identification of the matrix representation of the reaction operator \hat{K} . The poles of the scattering matrix \underline{S} , obtainable from \underline{K} using the procedure of Breit and Wigner,⁵ then give the resonance energy and width as defined by Mandl¹⁶ and Seigert.¹⁷

Recently we briefly reported¹⁸ the results of an application of the CI formalism to the $(nl^2)^{1S}$ states of He with $n=2-4$, $l \leq 2$ and $n=5$, $l=0$ with energies in the range 57.96–75.51 eV above the ground state (i.e., the region in which the $n=1-3$ channels are open). We present these results more fully and with corrections in Sec. III.

Neutral atoms support an infinite number of Rydberg series of autoionizing states since a positive ion has a long-range attractive Coulomb potential for an electron. Helium is the simplest system having this property and hence is an attractive object of calculations. Each nl^2 state is the lowest member of a Rydberg series. In all the experimental and theoretical studies of He, resonances from only the first few series have been considered. Experimentally, no resonances above the $n=4$ threshold and only three states above the $n=3$ threshold have been observed.¹⁹ Only the quasivariational techniques have been attempted on states above the $n=3$ threshold.²⁰⁻²²

As n increases, the spacings between adjacent levels decrease and hence one would expect that at some large n the effects of near-neighbor resonance interactions will be important. The effects of near-neighbor interactions of closely lying or overlapping resonances in scattering have been considered by Mies,²³ Breit and Wigner,⁵ and Feshbach.²⁴ In scattering theory a resonance is the solution of the Schrödinger equation with normal-scattering boundary conditions at a complex energy $E = E^r + i\Gamma$ such that the scattering amplitude possesses a pole.^{16, 25} By its nature, the CI formalism more directly gives the resonance energy and width from the Feshbach approach.^{16, 26} This approach defines the autoionizing state as being bound, with respect to some ionization threshold, by an energy ϵ . Upon coupling to a degenerate continuum the autoionizing state becomes a decaying state of energy $E^r = \epsilon + \Delta$ with width Γ . Γ is proportional to the magnitude of the interaction between the bound and continuum states, and Δ is the energy shift associated with

this interaction. The effects of near-neighbor interactions, discussed more fully in Sec. II B, are the distinguishing factor between the Feshbach and Seigert approaches. We consider, in Sec. III D, the resonant interaction effects of the higher resonances in helium.

One further aspect of the higher resonances prompts a more complete investigation. In the Hartree-Fock²¹ atom, as n increases the ns^2 energy approaches the next lowest threshold [the energy of the $(n-1)$ state of He^+] and at $n \geq 7$ actually falls below it. Therefore, for $n \geq 7$, ionization is accompanied with a change in principal quantum number of two [$ns^2 - (n-2)sk$] or more by the target electron. As one proceeds to the correlated system (e.g., many bound configurations) one might expect this phenomenon to occur at some other value of principal quantum number n . Indeed, for the atom in which the electrons do not interact at all, it is easily seen that the $4s^2$ state cannot decay to the $3sks$ state. No violation of the Wigner-Von Neuman noncrossing rule is involved here, since the rule assumes the interaction of two stationary states having real energies. However, in our case one state is a continuum and the other is nonstationary with a complex energy. Mandl²⁷ has shown that noncrossing rules apply for complex energy curves but this still implies that the real parts of the energies can cross provided the imaginary parts are different at the crossing point. What happens to the width of the ns^2 resonance because of the closing of the $(n-1)$ channels can be determined only by a more complete calculation. These effects are considered in Sec. III B.

II. FORMAL CI THEORY

A. Solution of CI equations

The task of the CI theory is to determine the wave function Ψ_{jE} by evaluating the coefficients a_n and $b_{m\epsilon}$ of the linear expansion

$$\Psi_{jE}(\vec{r}, \vec{r}') = \sum_n^N a_n(jE)\phi_n(\vec{r}, \vec{r}') + \sum_m^M \int b_{m\epsilon}(jE)\psi_{m\epsilon}(\vec{r}, \vec{r}') d\epsilon, \quad (1)$$

such that the full Hamiltonian is diagonalized;

$$\langle \Psi_{jE} | H | \Psi_{iE'} \rangle = E \delta_{ij} \delta(E - E'). \quad (2)$$

In Eq. (1) ϕ_n denotes the discrete configurations and $\psi_{m\epsilon}$ the continuum configurations at energy ϵ . The subscripts j and E denote the state, \vec{r} gives the coordinates of the incident electron, and \vec{r}' denotes those of the electrons on the target

atom. We write the matrix elements

$$\langle \phi_n | \phi_{n'} \rangle = \delta_{nn'} + S_{nn'}, \quad (3a)$$

$$\langle \phi_n | H | \phi_{n'} \rangle = \epsilon_n^0 \delta_{nn'} + V_{nn'}, \quad (3b)$$

$$\langle \phi_n | \psi_{m\epsilon} \rangle = S_{nm\epsilon}, \quad (3c)$$

$$\langle \phi_n | H | \psi_{m\epsilon} \rangle = V_{nm\epsilon}, \quad (3d)$$

$$\langle \psi_{m\epsilon} | \psi_{m'\epsilon'} \rangle = \delta_{mm'} \delta(\epsilon - \epsilon') + S_{m\epsilon m'\epsilon'}, \quad (3e)$$

$$\langle \psi_{m\epsilon} | H | \psi_{m'\epsilon'} \rangle = \epsilon \delta_{mm'} \delta(\epsilon - \epsilon') + V_{m\epsilon m'\epsilon'}, \quad (3f)$$

where for later convenience S and V represent small residual quantities in both the diagonal and nondiagonal cases.

The application of the CI theory to autoionizing states necessarily implies that some of the discrete configurations are degenerate with some of the continua, thus introducing a singularity. To obviate this singularity, Fano¹ defines a new coefficient $d_{m\epsilon}(jE)$ by

$$b_{m\epsilon}(jE) = \hat{P} \frac{1}{E - \epsilon} d_{m\epsilon}(jE) + \delta(E - \epsilon) Z_m(jE), \quad (4)$$

$$\bar{K}_{nm\epsilon}^{QP} = V_{nm\epsilon} - ES_{nm\epsilon} + \sum_{m'} \hat{P} \int \frac{(V_{nm'\epsilon'} - ES_{nm'\epsilon'}) \bar{K}_{m'\epsilon'm\epsilon}^{PP}}{E - \epsilon'} d\epsilon', \quad (8)$$

$$\bar{K}_{m\epsilon n}^{PQ} = V_{m\epsilon n} - ES_{m\epsilon n} + \sum_{m'} \hat{P} \int \frac{(V_{m\epsilon m'\epsilon'} - ES_{m\epsilon m'\epsilon'}) \bar{K}_{m'\epsilon'n}^{PQ}}{E - \epsilon'} d\epsilon', \quad (9)$$

$$\bar{K}_{m\epsilon m'\epsilon'}^{PP} = V_{m\epsilon m'\epsilon'} - ES_{m\epsilon m'\epsilon'} + \sum_{m''} \hat{P} \int \frac{(V_{m\epsilon m''\epsilon''} - ES_{m\epsilon m''\epsilon''}) \bar{K}_{m''\epsilon'm'\epsilon'}^{PP}}{E - \epsilon'} d\epsilon'', \quad (10)$$

and

$$\bar{K}_{i_n}^{QQ} = V_{i_n} - ES_{i_n} + \sum_{m'} \hat{P} \int \frac{(V_{i_m'\epsilon'} - ES_{i_m'\epsilon'}) \bar{K}_{m'\epsilon'n}^{PQ}}{E - \epsilon'} d\epsilon'. \quad (11)$$

Equations (7)–(11) are simply an alternative expression of the original problem [Eq. (1) and (2)]. The integral equations have a striking similarity to the operator equation for the reaction matrix \underline{K} ,

$$\hat{K} = \hat{V} + \hat{P} \hat{V} \frac{1}{E\hat{1} - \hat{H}^0} \hat{K}, \quad (12)$$

as derived from the formal Lippmann-Schwinger scattering theory⁷ with $\hat{H} = \hat{H}^0 + \hat{V}$, and \hat{P} denoting the Cauchy principal part. Indeed the matrices \bar{K}^{PP} , \bar{K}^{PQ} , \bar{K}^{QP} , and \bar{K}^{QQ} can be interpreted as just the matrix representations of the operators $P\hat{K}P$, $P\hat{K}Q$, $Q\hat{K}P$, and $Q\hat{K}Q$ in the basis of the original configurations.¹⁵ The operators P and Q are the Feshbach projection operators, the P operator projecting onto the continuum configurations and $Q = 1 - P$. Equation (7) is the complete reaction matrix including the singular term which is responsible for the observed reso-

where $Z_m(jE)$ is an integration constant to be determined by normalization and \hat{P} means the Cauchy principal part, which is to be taken in integrals arising when Eq. (4) is substituted into Eqs. (1) and (2). The resulting equations can be solved following the procedure of Fano and Prats⁶ for continuum states (the presence of the bound configurations is not a significant complication) giving for the coefficients the expressions

$$a_n(jE) = - \sum_m^M \sum_i^N [(\bar{K}^{QQ} - \epsilon^0 - E\hat{1})^{-1}]_{ni} \times \bar{K}_{i_m\epsilon}^{QP} Z_m(jE). \quad (5)$$

and

$$d_{m\epsilon}(jE) = \sum_{m'}^M K_{m\epsilon m'\epsilon'}^{PP} Z_{m'}(jE), \quad (6)$$

where we have defined

$$\underline{K}^{PP} = \bar{K}^{PP} + \bar{K}^{PQ}(E\hat{1} - \epsilon^0 - \bar{K}^{QQ})^{-1} \bar{K}^{QP}, \quad (7)$$

nances.

The integration constants $Z_m(jE)$ [Eqs. (5) and (6)] can be related to the phase shift induced by the interactions among the configurations $\psi_{m\epsilon}$ and ϕ_n ,^{6,15}

$$\bar{\delta}_n(jE) + \delta_n^r(jE) = \tan^{-1} \left(\frac{-\pi \sum_{m'}^M K_{m\epsilon m'\epsilon'}^{PP} Z_{m'}(jE)}{Z_n(jE)} \right). \quad (13)$$

$\bar{\delta}_n(jE)$ represents the contribution to the phase shift induced by the residual potential [V , Eq. (3f)] and arises solely from the mixing of the continuum functions, whereas $\delta_n^r(jE)$ is the resonant part of the phase shift owing to the interaction with the bound configurations. When physical conditions establish the proper asymptotic representation, the phase shift is determined, and Eq. (13) determines the constants $Z_m(jE)$.

Electron scattering is described conveniently

by the incoming wave form,

$$\Psi_{jE}^- \sim \sum_m^M c_m(\vec{r}') \frac{1}{r} \frac{(-i)}{(2\pi k_m)^{1/2}} \times (e^{i\Theta_{mE}} S_{mj} - \delta_{mj} e^{-i\Theta_{mE}}), \quad (14)$$

involving the scattering matrix S_{mj} , where $k_n = \{2\epsilon + [(z-1)/n]^2\}^{1/2}$ is the linear momentum of the electron in the n th channel,

$$\Theta_{n\epsilon} = k_n r + \frac{z-1}{k_n} \ln(2k_n r) - \frac{1}{2}\pi l, \quad (15)$$

$c_n(\vec{r}')$ includes the target eigenfunction and the angular part of the total wave function (all factors irrelevant in this consideration), z is the nuclear charge, and l is the orbital angular-momentum quantum number of the incident electron. With this choice for the asymptotic representation Mies²³ obtains the following expressions for the constants \underline{Z} :

$$\underline{1} = [(\underline{S}^0)^{1/2}]^* (\underline{1} + i\pi \underline{K}^{PP}) \underline{Z}, \quad (16a)$$

$$\underline{S} = (\underline{S}^0)^{1/2} (\underline{1} - i\pi \underline{K}^{PP}) \underline{Z}, \quad (16b)$$

where \underline{S}^0 is a diagonal matrix with $S_{n\epsilon}^0 = \exp(2i\delta_{n\epsilon}^0)$, and $\delta_{n\epsilon}^0 = -\arg \Gamma(l+1+i(z-1)/k_n)$ is the phase shift of the initial functions,

$$\psi_{n\epsilon}(\vec{r}, \vec{r}') \sim c_n(\vec{r}') \frac{1}{r} \left(\frac{2}{\pi k_n}\right)^{1/2} \sin(\Theta_{n\epsilon} + \delta_{n\epsilon}^0). \quad (17)$$

Inversion of $[(\underline{S}^0)^{1/2}]^* (\underline{1} + i\pi \underline{K}^{PP})$ gives \underline{Z} and defines the scattering matrix in terms of the reaction matrix \underline{K} by the usual relation,

$$\underline{S} = (\underline{S}^0)^{1/2} (\underline{1} - i\pi \underline{K}^{PP}) (\underline{1} + i\pi \underline{K}^{PP})^{-1} (\underline{S}^0)^{1/2}. \quad (18)$$

B. Determination of the resonant reaction matrix, widths energies, and cross sections

The determination of the normalization constants $Z_m(jE)$ gives the final wave function Ψ_{jE} but not the resonance widths and energies. We need to obtain the reaction matrix \underline{K}^r due just to the resonances. In Eq. (13) we distinguished between the nonresonant $\delta_m(jE)$ and resonant $\delta_m^r(jE)$ parts of the total phase shift. Upon excluding all discrete states in the CI, the resulting reaction matrix is just \underline{K}^{PP} , the nonresonant reaction matrix. Knowledge of the total residual reaction matrix \underline{K}^{PP} , Eq. (7), and the nonresonant part \underline{K}^{PP} allows us to evaluate \underline{K}^r directly giving,

$$\underline{K}^r = -\underline{Y}^+ (\underline{\epsilon}^0 - E \underline{1} + \underline{K}^{QQ})^{-1} \underline{Y} [\underline{1} - i\pi \underline{K}^{PP} \underline{Y}^+ \times (\underline{\epsilon}^0 - E \underline{1} + \underline{K}^{QQ})^{-1} \underline{Y}]^{-1}, \quad (19)$$

where to simplify notation we have introduced the expression

$$\underline{Y} = \underline{K}^{QP} [\underline{1} + (\pi \underline{K}^{PP})^2]^{-1/2}. \quad (20)$$

Rearrangement to a more symmetric form utilizing a procedure similar to that employed by Breit and Wigner⁵ for rearranging S^r gives

$$\underline{K}^r = -\underline{Y}^+ \underline{S}^{-1/2} [\underline{S}^{-1/2} (\underline{\epsilon}^0 + \underline{K}^{QQ} + \pi \underline{F}) \underline{S}^{-1/2} - E \underline{1}]^{-1} \underline{S}^{-1/2} \underline{Y}, \quad (21)$$

where $\underline{F} = -\pi \underline{Y} \underline{K}^{PP} \underline{Y}^+$. Diagonalization of the expression in square brackets, such that

$$\underline{D} = \underline{S}^{-1/2} (\underline{\epsilon}^0 + \underline{K}^{QQ} + \pi \underline{F}) \underline{S}^{-1/2} = \underline{U} \underline{E}^r \underline{U}^+, \quad (22)$$

and defining

$$\underline{C} = \underline{S}^{-1/2} \underline{U} \quad (23)$$

and

$$\nu_{n\alpha} = [\underline{C}^+ \underline{Y}]_{n\alpha} = [\underline{C}^+ \underline{K}^{QP} (\underline{1} + (\pi \underline{K}^{PP})^2)^{-1/2}]_{n\alpha}, \quad (24)$$

gives

$$K_{\alpha\beta}^r = \sum_n^N \frac{\nu_{n\alpha}^* \nu_{n\beta}}{E - E_n^r}, \quad (25)$$

the familiar form for \underline{K}^r .^{23,28} We identify the partial widths $\Gamma_{n\alpha}$ as $2\pi |\nu_{n\alpha}|^2$ and the resonance energies E_n^r as the eigenvalues of \underline{D} .

The net effect of the integrals in Eq. (22) is to introduce coupling among the zero-order bound states owing to interactions with each other and to their mutual interactions with the continua (represented by the \underline{K}^{QQ} and \underline{F} terms). These interactions produce shifts in the resonances according to the Feshbach definition. Mies²³ has defined a new set of shifted resonance states ϕ_n^s ,

$$\phi_n^s = \sum_m [\underline{C}^+]_{nm} \phi_m, \quad (26)$$

which diagonalize these interactions giving energies E_n^r .²³ Since \underline{K}^{PP} provides for the complete coupling among the zero-order continuum functions $\psi_{m\epsilon}$ in the absence of any bound states, Mies similarly defines a set of intermediate continuum functions Ψ_{iE}^I which diagonalize these interactions at energy E ,

$$\Psi_{iE}^I = \hat{P} \int \sum_m^M \frac{\psi_{m\epsilon}}{E - \epsilon} [(\underline{K}^{PP} + \delta(E - \epsilon) \underline{1}) \times (\underline{1} + (\pi \underline{K}^{PP})^2)^{-1/2}]_{mi} d\epsilon. \quad (27)$$

Equation (35) can then be written

$$\nu_{n\alpha} = \langle \phi_n^s | H - E | \Psi_{\alpha E}^I \rangle_{E=E_n^r}. \quad (28)$$

Therefore $\nu_{n\alpha}$ is the interaction of the n th resonance state ϕ_n^s with the continuum ψ_{IE}^I in accord with the Feshbach definition.

We can relate Eq. (28) here to the "golden rule" type formula recently proposed by Miller,⁹

$$\Gamma_{n\alpha} = 2\pi |\langle \phi_n | H - E | \chi_{\alpha E} \rangle|^2, \quad (29)$$

where the α th partial wave of the continuum function χ is simply

$$\chi_{\alpha E} = \left(\frac{2\mu}{\pi k} \right)^{1/2} \frac{i^\alpha}{\gamma} e^{i\delta_0} \sin(kr + \epsilon_0 - \frac{1}{2}\pi\alpha), \quad (30)$$

and where $k^2 = 2\mu E$. Miller used the operator $H - E$ instead of H to remove the restriction that $\chi_{\alpha E}$ be orthogonal to ϕ_n . Also Miller showed that if ϕ_n is a good approximation (apart from a multiplicative constant) to the exact scattering function Ψ_{jE} in the interaction region, and if the phase shift ϵ_0 of $\chi_{\alpha E}$ is the same as the nonresonant potential scattering phase shift, then Eq. (29) yields the correct width.⁹ All of these conditions are met by Eq. (28). With enough discrete configurations, ϕ_n^s can approximate the short-range part of the exact scattering function to any degree of accuracy, and the intermediate continuum ψ_{IE}^I has the asymptotic form of Eq. (30) with the proper phase shift. This suggests that, provided one includes the asymptotically correct continuum functions, one should concentrate on optimizing the discrete part of the function in the interaction region to obtain the best widths.

By defining a relative partial width $\gamma_{n\alpha} = \Gamma_{n\alpha} / \sum_{\alpha'} \Gamma_{n\alpha'}$, the total width $\Gamma_n = \sum_{\alpha} \Gamma_{n\alpha}$ can be given by

$$\begin{aligned} \Gamma_n &= 2\pi |\langle \phi_n^s | H - E | \sum_{\alpha} \gamma_{n\alpha} \psi_{\alpha E}^I \rangle|^2 \\ &= 2\pi \langle \phi_n^s | H - E | \Psi_{nE}^I \rangle^2, \end{aligned} \quad (31)$$

where the linear combination of continua,

$$\Psi_{nE}^I = \sum_{\alpha} \gamma_{n\alpha} \psi_{\alpha E}^I, \quad (32)$$

embodies the total configuration interaction between the n th resonance and the M open channels.²³ There are $M - 1$ remaining orthonormal continua, Ψ_{mE}^I , $m = 2, 3, \dots, M$, which are orthogonal also to ϕ_n^s and give rise to potential or background contributions to the over-all scattering. The Ψ_{nE}^I functions of different n are not necessarily orthogonal and Mies²³ defines an overlap matrix Θ , by the equation

$$\begin{aligned} \langle \Psi_{nE}^I | \Psi_{mE}^I \rangle &= \delta(E - E') \Theta_{nm} \\ &= \delta(E - E') \sum_{\alpha} \gamma_{n\alpha} \gamma_{m\alpha}. \end{aligned} \quad (33)$$

The resonant scattering matrix \underline{S}^r can be obtained from Eq. (25) using the rearrangement procedure of Breit and Wigner,⁵

$$S_{\alpha\beta}^r = \delta_{\alpha\beta} - \sum_n \frac{\gamma_{n\alpha}^* i \Gamma_{n\beta}^e \nu_{n\beta}}{E - E_n^e + \frac{1}{2} i \Gamma_n^e}, \quad (34)$$

where

$$E_n^e = \frac{\sum_m^N E_m^r |G_{mn}|^2}{\sum_m^N |G_{mn}|^2} \quad (35)$$

and

$$\Gamma_{n\alpha}^e = 2\pi \frac{|\sum_m^N [G^+]_{nm} \nu_{m\alpha}|^2}{\sum_m^N |G_{mn}|^2}. \quad (36)$$

The parameters Γ_n^e and E_n^e are termed the "effective" width and resonance energy and hence we append the superscript "e" to the corresponding variables. The matrix \underline{G} is a complex orthogonal matrix defined by

$$\gamma_{n\alpha}^e = \left(\frac{2\pi}{\Gamma_n^e} \right)^{1/2} \sum_m^N [G^+]_{nm} \nu_{m\alpha} \quad (37)$$

and diagonalizes the interaction matrix between neighboring resonances.

The same rearrangement procedure applied to the total scattering matrix [Eq. (18)] gives the total cross section

$$\begin{aligned} \sigma(E)(\alpha - \beta) &= \frac{\pi(2L+1)(2S+1)}{2k_\alpha^2(2I_\alpha+1)} \\ &\times \left| T_{\alpha\beta}^P + \sum_n \frac{g_{\alpha n} - i \Gamma_n^e g_{n\beta}}{E - E_n^e + \frac{1}{2} i \Gamma_n^e} \right|^2, \end{aligned} \quad (38)$$

where α and β indicate the incident and scattered channels, k_α is the wave number of the incident electron, L and S are the total angular momentum and spin of the system, and $\underline{g} = \gamma \underline{S}^{1/2} (\underline{S}^0)^{1/2}$. The total cross section consists of a contribution from each resonance plus a nonresonant part accounted for by the matrix \underline{T}^P . The parameter $|g_{n\beta}|^2$ is the relative probability that the n th resonance decays to the β th channel.

Using the Fano-Cooper^{2,3,29} profile parameters, the fundamental line-shape formula,

$$\sigma(E)(\alpha - \beta) = \sigma_b^n (\alpha - \beta) + \sigma_a^n (\alpha - \beta) \frac{(\epsilon^n + q_{\alpha\beta}^n)^2}{1 + (\epsilon^n)^2}, \quad (39)$$

is obtained where $\epsilon^n = 2(E - E_n^e)/\Gamma_n^e$, $q_{\alpha\beta}^n$ is the shape parameter, and σ_a^n and σ_b^n represent, respectively, the resonant and nonresonant parts of the total cross section. A parameter $\rho_{\alpha\beta}^n = [\sigma_a^n / (\sigma_a^n + \sigma_b^n)]^{1/2}$ has been introduced by Fano and Cooper^{2,3} and is interpreted as the correlation coefficient

between the state reached by direct excitation and the state reached by resonant excitation.

Equations (25) and (34) give the energy dependence of \underline{K}^r and \underline{S}^r explicitly, provided $E_n^r, E_n^{re}, \Gamma_n$, and Γ_n^e vary slowly with E .²³ The representation for \underline{K}^r involves the fundamental parameters $\Gamma_{n\alpha}$ and E_n^r which are shown by Eqs. (22) and (24) to be defined in accordance with the Feshbach viewpoint. The quantities E_n^{re} and $\Gamma_{n\alpha}^e$ are the fundamental parameters in the Seigert approach, since at the complex energy $E = E_n^{re} + i\Gamma_n^e$ the scattering amplitude has a pole and the "everywhere outgoing-wave boundary condition"¹⁶ on the scattering state is satisfied. The relations between E_n^r and E_n^{re} and $\Gamma_{n\alpha}$ and $\Gamma_{n\alpha}^e$ in Eqs. (35) and (36) show that the two definitions are identical for an isolated resonance, a conclusion also reached by Mandl¹⁶ using second-order perturbation theory. For closely lying resonances ($|E_n^r - E_{n-1}^r| \leq \frac{1}{2}\Gamma_n$) the two definitions are identical only when \bar{G} is real or when the matrix $\underline{\nu}^+ \underline{\nu}$ is diagonal. From Eq. (33), this is true only when $\bar{\Theta}$ is diagonal. Θ_{nm} has been interpreted as the overlap of the continua to which the n th and m th resonances couple or autoionize. Hence resonances which couple to orthogonal continua do not "overlap" or interact with another, and the widths and energies obtained from the two definitions are equal. When neighboring resonances decay to nonorthogonal continua the widths and resonance energies defined by the two approaches may not correspond.²³

III. APPLICATION TO He

A. Computational considerations

The choice of basis functions in the application of the CI theory to the $(nl^2)^1S$ states of He is motivated partly by convenience. From the arguments of Miller⁹ discussed in Sec. II B, the continuum functions need be correct only in the asymptotic region, provided the discrete functions ϕ_n adequately approximate the scattering function in the interaction region. With this in mind we use for the continua, $\psi_{m\epsilon}$, a symmetrized product of screened hydrogenic orbitals (spin functions are suppressed throughout this section):

$$\begin{aligned} \psi_{m\epsilon} = & \psi_{n1}(z=2, r_1) \psi_{k1}(z=1, r_2) \\ & \pm \psi_{n1}(z=2, r_2) \psi_{k1}(z=1, r_1). \end{aligned} \quad (40)$$

Assuming the long-range distortion is negligible in the presence of the Coulomb field, the asymptotic behavior of $\psi_{m\epsilon}$ is exact to within a constant phase shift and this is corrected by the CI treatment.

The necessary bound functions for ϕ_n can be obtained by any of the quasivariational procedures.⁴

Again for convenience, in this application we use a product of orbitals,

$$\phi_n = \psi_{n1}(r_1) \psi_{n1}(r_2). \quad (41)$$

Calculations were performed using both the hydrogenic orbitals and Hartree-Fock orbitals for ψ above. The results using hydrogenic orbitals were less satisfactory³⁰ so only the Hartree-Fock results are given here. Our method for obtaining the Hartree-Fock orbitals has been reported previously.²¹

The basic numerical problem in employing the CI theory is to construct the matrices $\underline{K}^{QQ}, \underline{K}^{QP}, \underline{K}^{PQ}$, and \underline{K}^{PP} . Of these, \underline{K}^{PP} and \underline{K}^{QP} require the solutions to a set of coupled integral equations. All of the energy and overlap matrix elements, Eq. (3), are obtained by procedures previously described.^{30,31} Other somewhat similar techniques have been given.³²⁻³⁵ The Cauchy integrals are evaluated numerically by the procedure of Altick and Moore.¹³ The infinite limit on these integrals is reduced to some finite limit ϵ_{\max} consistent with the accuracy in the evaluation of the Coulomb matrix elements.^{30,31}

The quantities $E_n^r, E_n^{re}, \Gamma_n$, and Γ_n^e are slowly varying functions of E over the energy range $E_n^r \pm \frac{1}{2}\Gamma_n$. To determine the corresponding energy-independent quantities $\bar{E}_n^r, \bar{E}_n^{re}, \bar{\Gamma}_n$, and $\bar{\Gamma}_n^e$, which represent the fundamental properties of the resonance state, we apply a least-squares curve-fitting technique³⁶ to the equations

$$\begin{aligned} \eta_0 + \eta_1 E + \tan^{-1}[\frac{1}{2}\bar{\Gamma}_n/(E - \bar{E}_n^r)] \\ = \tan^{-1}\{\frac{1}{2}\Gamma_n(E)/[E - E_n^r(E)]\} \end{aligned} \quad (42)$$

and

$$\begin{aligned} A + BE + \frac{C}{(E - \bar{E}_n^{re})^2 + (\frac{1}{2}\bar{\Gamma}_n^e)^2} \\ = \frac{[\frac{1}{2}\Gamma_n^e(E)]^2}{[E - E_n^{re}(E)]^2 + [\frac{1}{2}\Gamma_n^e(E)]^2}. \end{aligned} \quad (43)$$

These represent the phase shift and Breit-Wigner line shapes (see Fig. 1). The parameters η_0, η_1, A , and B above account for any nonresonant behavior. The energy-independent partial widths $\bar{\Gamma}_{n\alpha}$ and $\bar{\Gamma}_{n\alpha}^e$ are obtained by Lagrangian interpolation of the points $\Gamma_n(E)$ and $\Gamma_n^e(E)$ at the energy \bar{E}_n^r and \bar{E}_n^{re} , respectively.

One practical advantage of the CI treatment is that a single calculation at some reasonable energy E determines all the energies and widths of the resonances accurate to within the range of variation of $E_n^r(E)$ and $E_n^{re}(E)$. Thus the CI technique greatly reduces the search procedure which in regions of closely lying resonances could be prohibitively time consuming. Elaborate search pro-

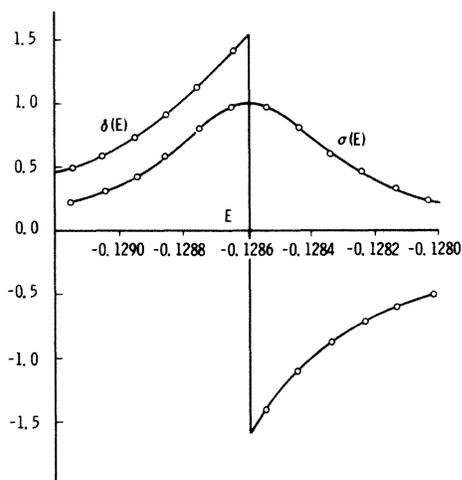


FIG. 1. Fit of phase shift and Breit-Wigner line shapes, Eq. (42) and (43), to the calculated points for the $5s^2$ state.

cedures have been necessary³⁷ when using some other techniques not sharing this advantage.

Table I indicates those bound configurations ϕ_n included in the calculation for each resonance. The coefficients C_{nm} are those in Eq. (23) evaluated at or very near \tilde{E}_n^r . From these coefficients we determine a spectroscopic designation for each level following Lipsky and Russek³⁸ and Ormonde, Whitaker, and Lipsky.³⁹ The notation is used with less validity however above $n=3$. The second column in Table I gives the level designation, the first column gives the configuration from the independent-particle model which correlates with each state according to the position within each cluster of the same n . Using the Hartree-Fock configura-

tions indicated in Table I, the calculations converged satisfactorily at least for the lower l states. The addition of $n'l^2(n' > n+1)$ configurations was not tested; however, they should have a very small effect. The configurations $nl'n'l$ ($n' > n$) should also have a small effect because of Brillouin's theorem.⁴⁰ Similar calculations using hydrogenic configurations did not converge as satisfactorily, indicating the effect of optimizing the configurations. Tables indicating the convergence of both the hydrogenic and Hartree-Fock results have been given elsewhere.³⁰ All calculations were limited to a maximum of ten bound-state configurations.

B. Energies and widths of the $(nl^2)^1S$ states

In Table II, we list our calculated positions and widths and compare them with a selection of those in the literature. A complete bibliography of previous results has already been given.³⁰ Despite the relatively large uncertainties indicated in our widths, the agreement with other work is very satisfactory. The widths of the nm^- states (the $nmnd^-$ and $nmnf^+$ states also contain components of nm^-) may be particularly uncertain because as indicated by Eq. (21) they are the (sometimes small) difference between larger quantities (i.e., the width of the nm^- state in the limit of strong coupling is the difference between the geometric and arithmetic means of the widths of the ns^2 and np^2 configurations). The CI technique is not unique in this regard; we expect similar difficulties in other techniques as well. This is true of all states characterized by a linear combination of one-electron orbitals coupled strongly with opposite signs.

Our resonance energies are consistently slightly higher than those obtained by the close-coupling

TABLE I. Resonant-state eigenvectors (bound part) of the $(nl^2)^1S$ autoionizing states of He below the $n=4$ threshold. [Coefficients C_{nm} in Eq. (23) evaluated at or near the resonance energy \tilde{E}_n^r . The Hartree-Fock orbitals are given in Ref. 21.]

State	Level designation	\tilde{E}_n^r (eV)	$2s^2$	$2p^2$	$3s^2$	$3p^2$	$3d^2$				
$2s^2$	22+	57.99	0.856	0.519	-0.0381	-0.0626	0.00556				
$2p^2$	22-	63.16	0.507	-0.851	-0.0433	0.142	-0.132				
			$3s^2$	$3p^2$	$3d^2$	$4s^2$	$4p^2$	$4d^2$	$4f^2$		
$3s^2$	33+	69.44	0.751	0.642	0.163	-0.0380	-0.0689	-0.0307	0.000339		
$3p^2$	333d ⁻	70.50	0.535	-0.455	-0.718	-0.0349	0.0582	0.138	-0.0364		
$3d^2$	333d ⁺	72.75	0.358	-0.583	0.648	-0.0535	0.0904	-0.218	0.322		
			$4s^2$	$4p^2$	$4d^2$	$4f^2$	$5s^2$	$5p^2$	$5d^2$	$5f^2$	
$4s^2$	44+	73.58	0.687	0.677	0.265	0.0443	-0.0388	-0.0743	-0.0408	-0.0123	
$4p^2$	444d ⁻	73.95	0.516	-0.210	-0.768	-0.332	-0.0334	0.0292	0.121	0.0774	
$4d^2$	444f ⁺	74.61	0.402	-0.497	0.106	0.775	-0.0363	0.0686	-0.0335	-0.218	
$5s^2$	55+	75.51	0.00155	-0.0222	-0.0260	-0.00127	0.638	0.690	0.339	0.0736	

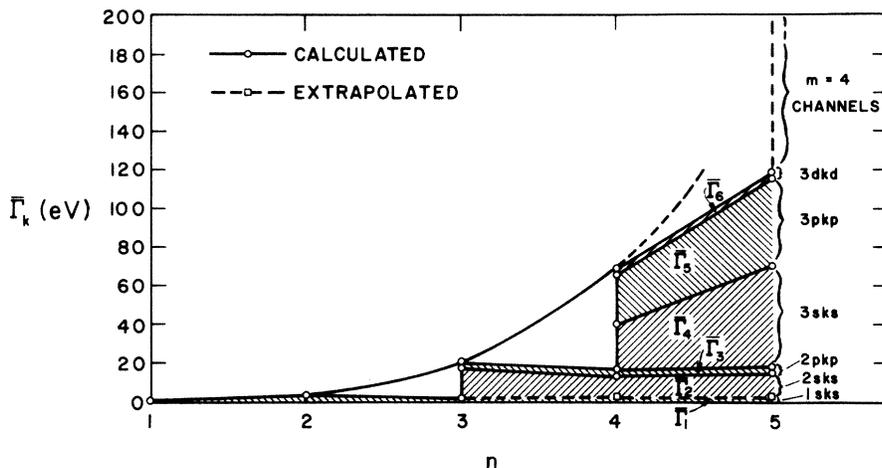


FIG. 2. Reduced total width $\bar{\Gamma}_k$ vs n , the principal quantum number of the ns^2 (nn^+) resonance states. Only the points are physically significant. Estimations or extrapolations are indicated by dotted lines.

the major contribution to the matrix element $\langle n'lnl | r_{12}^{-1} | mkl \rangle$ for the width $\bar{\Gamma}_{nk}$ comes from the interaction region. Since for large n , the hydrogenic orbitals at small r change only by a normalizing constant proportional to $n^{-3/2}$, they argued that the quantity $(n-d)^3 \bar{\Gamma}_{nk}$ should be approximately independent of n . Thus they conclude that the relationship among partial widths of successive states of Rydberg series is given approximately by $\bar{\Gamma}_k = \frac{1}{2}(n-d)^3 \bar{\Gamma}_{nk}$, where d is the quantum defect defined by $\bar{E}_n^r = -Z^2/(n-d)^2$. $\bar{\Gamma}_k$ is called the reduced width and is approximately constant for all members of a series decaying to the k th channel. For our system, we conclude that the widths for the lowest nl^2 state in each Rydberg series is given by $\bar{\Gamma}_k = \frac{1}{4}(n-d)^6 \bar{\Gamma}_{nk}$. Figure 2 reveals that $\bar{\Gamma}_k$ is indeed reasonably constant for each of the partial widths of the ns^2 states. However, the total reduced width $\bar{\Gamma} = \sum_k \bar{\Gamma}_k$ varies approximately exponentially because of the increased number of open channels for each higher state.

The $4f^2$ state was found to be very near the $n=4$ threshold. Due to threshold effects which are not

accounted for in the CI theory, we did not reliably determine the $4f^2$ resonance parameters. The $5s^2$ state definitely lies below the $n=4$ threshold. Although it is evident the $m=3$ channels partially compensate for the closing of the $m=4$ channels, the effect on the width of the $5s^2$ is clearly visible from Fig. 2. The dotted curve is our estimate of the manner in which the reduced total width would increase if the $m=4$ channels were open.

Our computer codes are limited to five open channels, hence the $1sks$ channel was omitted from the $n=4$ and $n=5$ resonances. An extrapolation of $\bar{\Gamma}$ is indicated in Fig. 2. The error in omitting the $1sks$ channel as indicated by Fig. 2 is then about 3% for the $4s^2$ state and 2% for the $5s^2$ state. The error in the higher angular momentum states ($l > 0$) is even less.

C. 1S wave cross-section parameters

In Table III we give our results for the relative probability $|g_{n\alpha}|^2$ for decay to each channel as de-

TABLE III. Probability for decay of the $(nl^2)^1S$ autoionizing states to the degenerate $(nlkl)^1S$ open channels.

State	1sks	2sks	2pkp	3sks	3pkp	3dkd	$\bar{\Gamma}$ (eV)
$2s^2(22+)$	1.00						0.094 25
$2p^2(22-)$	1.00						0.002 762
$3s^2(33+)$	0.101	0.766	0.133				0.052 26
$3p^2(333d-)$	0.000 964	0.185	0.806				0.1130
$3d^2(333d+)$	0.004 67	0.245	0.751				0.044 88
$4s^2(44+)$	0.03 ^a	0.158	0.0508	0.352	0.378	0.0329	0.034 54
$4p^2(444d-)$	0.000 06 ^a	0.0227	0.106	0.304	0.218	0.350	0.038 28
$4d^2(444f+)$	0.002 ^a	0.0915	0.235	0.205	0.304	0.165	0.006 562
$5s^2(55+)$	0.02 ^a	0.101	0.0279	0.447	0.383	0.0250	0.015 62

^a Estimated values as determined by Fig. 2 for the ns^2 states or comparable figure for the np^2 and nd^2 states.

terminated by the total cross section, Eq. (38). Our estimates from Fig. 2 for $\bar{\Gamma}_1$, and its effect on the total width $\bar{\Gamma}_n$ is also indicated in Table III. Since we are considering just the 1S wave, only the $(nlkl)^1S$ open channels are available for decay in L - S coupling. The widths are repeated for convenience. It can be seen that the preferred decay mechanism involves the smallest change in principal quantum number of the helium ion for all states studied here. But during decay it is evident an interelectronic transfer of orbital angular momentum may often occur. Physically this is to be expected since during decay a large transfer of kinetic energy (linear momentum) between the incident and target electrons must also take place.

The Fano-Cooper cross section parameters q^n and ρ^n are given in Table IV. The magnitude of q is determined by the phase-shift difference between the resonant and nonresonant scattered waves, and determines the point $E - \bar{E}_n^r - \frac{1}{2}q^n\bar{\Gamma}_n$ at which the cross section reaches a minimum. The sign of q therefore determines whether the minimum is below or above the resonance energy. Comparison with the experiments⁴⁴ is inconclusive, however our results which indicate q is negative for the $n=2$ states do agree with the Fano-Cooper analysis.³ Our results also agree with the theoretical close-coupling results of Burke and Taylor⁴² and Ormonde *et al.*³⁹ which indicate all partial-wave contributions to $q_{1sks,2sks}^n$ are plus for all the $n=3$ levels. Mendez⁴⁶ has shown that as $\rho \rightarrow 0$, $\sigma(E)$ approaches the Lorentzian line shape, and q in the Fano parameterization becomes insensitive. Therefore in those instances when ρ is small the value of q has little physical meaning even though the Fano parameterization still satisfactorily describes $\sigma(E)$ near the resonance.

The correlation parameter ρ gives the ratio of the reduction of the total cross section at the min-

imum near the resonance (located at $\epsilon^n = -q^n$) compared with an energy infinitely far away from the resonance ($\epsilon = \pm\infty$).³ With only one channel accessible for decay of the $n=2$ levels, σ_b equals 0 and ρ^n is identically equal to unity. Table IV reveals that ρ^n in some instances is still very close to one for the $n=3$ levels which can decay via three channels. Physically, this means that these resonance states happen to decay into the same linear combination of states that are excited by electron impact directly from the ground state. The implications of such have been discussed by Macek and Burke²⁹ for the $n=3$ resonances in e^- - H scattering.

D. Components of the energy shift

In Table V we give the components of the total energy shift of the final resonance energy $\bar{E}_n^{r_e}$ from the single configuration Hartree-Fock energy ϵ_n . One obvious feature of Table V is that the shift due to the near-neighbor resonance interaction is several orders of magnitude smaller than either E_{corr} and Δ_n . Thus the near-neighbor resonance interactions for the resonances considered in this work are negligible and the Feshbach and Seigert approaches give the same resonance parameters. This is expected since we have found $\bar{\Gamma}_n \ll |\bar{E}_n^r - \bar{E}_{n-1}^r|$. Here E_n^r represents only those resonances explicitly considered in the CI, hence only the $(n\ell^2)^1S$ states. The presence of several $(nl'n')^1S$ configurations in the CI would enhance any interaction effects beyond that observed from Table V. However, since the positions of the $n=2$ and $n=3$ states agree well with experiment, any interaction effects must be small at this energy. Our results do indicate a general enhancement of interaction effects as n increases, and at still higher n they may become significant.

TABLE IV. 1S wave Fano-Cooper resonance profile parameters $q_{\alpha\beta}^n$ and $\rho_{\alpha\beta}^n$ for scattering from the incident channel $\alpha = 1sks$ to the outgoing channel $\beta = nlkl$ for the $n=2l^2$ and $n=3l^2$ autoionizing states. [The $1sks$ open channel was not included in the calculation for the resonances above the third threshold (see text). The uncertainties in these numbers are similar to those indicated for the widths in Table II.]

$nlkl$	n	$2s^2$	$2p^2$	$3s^2$	$3p^2$	$3d^2$
$1sks$	q	-1.26	-1.37	-2.21	-0.532	0.251
	ρ	1.00	1.00	0.260	0.192	0.161
$2sks$	q			1.26	0.0184	0.308
	ρ			1.00	0.758	0.688
$2pkp$	q			1.35	-50.0	-2.12
	ρ			0.998	0.0355	0.549

TABLE V. Components of the total energy shift $\bar{E}_n^{r_e} - \epsilon_n$.^a

State	E_{corr}^b (eV)	Δ_n^c (10^{-3} eV)	$\bar{E}_n^{r_e} - \bar{E}_n^r$ (10^{-5} eV)	$\bar{E}_n^{r_e} - \epsilon_n$ (eV)
$2s^2$	-1.446	3.676	2.991	-1.442
$2p^2$	1.100	-0.8380	-1.126	1.099
$3s^2$	-0.8533	-12.58	6.033	-0.8658
$3p^2$	-0.6005	-68.03	74.70	-0.6678
$3d^2$	0.8704	-3.754	-57.56	0.8660
$4s^2$	-0.5373	-0.4979	11.04	-0.5377
$4p^2$	-0.5575	-42.44	5.033	-0.5998
$4d^2$	-0.1458	-26.10	-3.687	-0.1719
$5s^2$	-0.3601	-4.000	-7.392	-0.3642

^a ϵ_n is the single-configuration Hartree-Fock energy.

^b $E_{\text{corr}} = E_n^{\text{CI}} - E_n^{\text{HF}}$ (CI result, bound states only) $-\epsilon_n$.

^c $\Delta_n = \bar{E}_n^r - E_n^{\text{CI}}$.

Column 3 of Table V reveals that, except for the $2s^2$ state, Δ is always negative. Previously Bhatia, Temkin, and Perkins⁴⁷ concluded Δ is always positive for the 1S states. They, however, obtained their values by comparing their eigenvalues of QHQ with the resonances energies obtained by Burke and Taylor⁴² using the close-coupling theory with correlation. An interesting state-dependence pattern for the sign of Δ has been

developing. For instance, Altick and Moore¹⁴ found from a calculation using hydrogenic configurations that Δ for the $^1P^+$ states is consistently negative, that for the $^1P^-$ states positive. Chung and Chen¹⁰ in the same system found the 1S states gave a negative Δ while for the 3S states Δ is positive. Our result is consistent with that of Chung and Chen since their variational approach to the Feshbach equations is similar to the CI technique.

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¹U. Fano, *Phys. Rev.* **124**, 1866 (1961).

²U. Fano and J. W. Cooper, *Rev. Mod. Phys.* **40**, 6441 (1968).

³U. Fano and J. W. Cooper, *Phys. Rev.* **137**, A1364 (1965).

⁴A complete review of the theoretical and experimental techniques applied to resonances has been given previously by one of us [D. E. Ramaker, thesis (University of Iowa, 1971) (unpublished)]. Other review articles include: K. Smith, *Rep. Prog. Phys.* **29**, 373 (1966); P. G. Burke, *Adv. Phys.* **14**, 521 (1965); P. G. Burke, *Adv. At. Mol. Phys.* **4**, 173 (1968); H. S. Taylor, G. V. Nazarov, and A. Golebiewski, *J. Chem. Phys.* **45**, 2872 (1966); J. C. Y. Chen, *Nucl. Instrum. Methods* **90**, 237 (1970); H. S. Taylor, *Adv. Chem. Phys.* **18**, 91 (1970); J. Midtdal, K. Aashamar, and E. Holoien, *Phys. Norv.* **5**, 177 (1971); C. Nicolaides, *Phys. Rev. A* **6**, 2078 (1972).

⁵E. P. Wigner, *Phys. Rev.* **70**, 606 (1946); **70**, 15 (1946); G. Breit, *Phys. Rev.* **69**, 472 (1946).

⁶U. Fano and F. Prats, *Proc. Nat. Acad. Sci. India A* **33**, 553 (1963).

⁷B. A. Lippmann and J. Schwinger, *Phys. Rev.* **79**, 469 (1950).

⁸E. Ressayre and R. Lefebvre, *Chem. Phys. Lett.* **8**, 553 (1971).

⁹W. H. Miller, *Chem. Phys. Lett.* **4**, 627 (1970); A. U. Hazi and M. F. Fels, *Chem. Phys. Lett.* **8**, 582 (1971); *Phys. Rev. A* **5**, 1236 (1972).

¹⁰K. T. Chung and J. C. Y. Chen, *Phys. Rev. Lett.* **27**, 1112 (1971); *Phys. Rev. A* **6**, 686 (1972).

¹¹A. Messiah, *Quantum Mechanics* (North-Holland, Amsterdam, 1966), p. 1005.

¹²V. V. Balashov, S. I. Grishanova, I. M. Kruglova, and V. S. Senashenko, *Opt. Spektrosk.* **28**, 859 (1970) [*Opt. Spectrosc.* **28**, 466 (1970)] relate the truncated diagonalization procedure (see Refs. 38 and 39) directly to an approximate Fano theory.

¹³P. L. Altick and E. N. Moore, *Phys. Rev.* **147**, 59

(1966).

¹⁴P. L. Altick and E. N. Moore, *Phys. Rev. Lett.* **15**, 100 (1965).

¹⁵F. Prats and U. Fano, in *Proceedings of the Third International Conference on the Physics of Electronic and Atomic Collisions*, edited by M. R. C. McDowell (North-Holland, Amsterdam, 1964), p. 600.

¹⁶F. Mandl, *Proc. Phys. Soc. Lond.* **90**, 913 (1967).

¹⁷A. J. F. Seigert, *Phys. Rev.* **56**, 750 (1939).

¹⁸D. E. Ramaker and D. M. Schrader, *J. Chem. Phys.* **55**, 471 (1971).

¹⁹R. P. Madden and K. Codling, *Astrophys. J.* **141**, 364 (1965).

²⁰R. B. Stevenson, thesis (University of Iowa, 1967) (unpublished).

²¹D. E. Ramaker, R. B. Stevenson, and D. M. Schrader, *J. Chem. Phys.* **51**, 5276 (1969).

²²E. Holoien and J. Midtdal, *J. Phys. B* **3**, 592 (1970); **4**, 32 (1971); and *Proceedings of the Seventh International Conference on the Physics of Electronic and Atomic Collisions* (North-Holland, Amsterdam, 1971), p. 1011; J. F. Perkins, *Phys. Rev. A* **2**, 1704 (1970).

²³F. H. Mies, *Phys. Rev.* **175**, 164 (1968).

²⁴H. Feshbach, *Ann. Phys. (N. Y.)* **43**, 410 (1967).

²⁵R. Yaris and R. Boehm, *J. Chem. Phys.* **55**, 1802 (1971).

²⁶H. Feshbach, *Ann. Phys. (N. Y.)* **5**, 357 (1958); **19**, 287 (1962).

²⁷F. Mandl, *Proc. Phys. Soc. Lond.* **87**, 871 (1966).

²⁸W. Brenig and R. Haag, *Fortschr. Phys.* **7**, 183 (1959).

²⁹J. H. Macek and P. G. Burke, *Proc. Phys. Soc. Lond.* **92**, 351 (1967).

³⁰D. E. Ramaker, thesis (University of Iowa, 1971) (unpublished).

³¹D. E. Ramaker, *J. Math. Phys.* **13**, 161 (1972).

³²F. E. Harris and H. H. Michels, *J. Comp. Phys.* **4**, 579 (1969).

³³R. K. Nesbet, *Phys. Rev.* **175**, 134 (1968).

³⁴C. Bottcher, *J. Comp. Phys.* **6**, 237 (1970).

³⁵J. D. Lyons and R. K. Nesbet, *J. Comp. Phys.* **4**, 499 (1969); **11**, 166 (1973).

³⁶M. J. Powell, *Comput. J.* **7**, 303 (1965).

³⁷R. K. Nesbet and J. D. Lyons, *Phys. Rev. A* **4**, 1812 (1971).

³⁸L. Lipsky and A. Russek, *Phys. Rev.* **142**, 59 (1966).

³⁹S. Ormonde, W. Whitaker, and L. Lipsky, *Phys. Rev. Lett.* **19**, 1161 (1967).

⁴⁰J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1963), Vol. I, p. 256.

⁴¹N. R. Daly and R. E. Powell, *Phys. Rev. Lett.* **19**, 1165

(1967).

⁴²P. G. Burke and A. J. Taylor, *J. Phys. B* 2, 44 (1969).

⁴³R. S. Oberoi, *J. Phys. B* 5, 1120 (1972).

⁴⁴Comparison with experiment is difficult because we consider just the 1S wave; the experiments give results for the sum of all partial waves. For example, the $(2s^2)^1S$ autoionizing states produce resonances only in the 1S wave, the remaining partial waves merely contribute to σ_b , thereby reducing ρ . Mendez (see text) has shown that as $\rho \rightarrow 0$, the resonance line shape becomes Lorentzian and the sign of q indeterminate. Recently P. Benoit-Cattin, D. Blanc, A. Bordenane-Montesquieu, A. Gleizes, M. Rodiere, and S. Solshanian, *J. Phys. E* 6, 564 (1973), obtained for the $2s^2$ state a value of $\rho^2 = 0.034$ and $q = 2.9 \pm 0.5$ by a curve fit

to the experimental cross section. However the experiments of J. A. Simpson, S. R. Mielizarek, and J. W. Cooper, *J. Opt. Soc. Am.* 54, 269 (1964), suggest if anything, that q is negative; experiments of Rudd, Simpson *et al.*, and Oda *et al.* (footnotes j, l, and m of Table II) suggest nothing about q since in all cases a nearly Lorentzian curve is observed. For the $3s^2$ state the experiments of Dance *et al.* (Ref. 45) suggest q is positive for the $1s-2s$ excitation cross section which agrees with theory.

⁴⁵D. F. Dance, M. F. A. Harrison, and A. C. H. Smith, *Proc. Phys. Soc. Lond. A* 290, 74 (1966).

⁴⁶A. J. Mendez, *J. Phys. B* 3, L39 (1970).

⁴⁷A. K. Bhatia, A. Temkin, and J. F. Perkins, *Phys. Rev.* 153, 177 (1967).