Resonance scattering theory: Application to the broad He⁻ $1s\,2s\,2p\,^2P^o$ resonance

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A resonance scattering theory for many-electron resonances is applied to the analysis of the He⁻ $1s\,2s\,2p\,^2P^o$ resonance. We have found that multiconfigurational Hartree-Fock theory is applicable even in such cases and predicts the Feshbach nature of the state. Furthermore, by including electron correlation and off-energy-shell pseudostates, we demonstrate the strong energy dependence of the width of this resonance. We suggest that this is the reason for the discrepancy of recent theoretical results with experimental ones. The theoretically predicted cross section is asymmetric, whereas the recent experimental one is symmetric but non-Lorentzian. Defining the position and width of the resonance at maximum and half-maximum values of the cross section correspondingly, we find $E_R = 20.26$ eV and $\Gamma_R = 600$ meV, compared to the experimental values of $E_R = 20.27$ eV and $\Gamma_R = 780$ meV.

I. INTRODUCTION

Electron scattering from He has attracted much theoretical and experimental attention during the past 20 years. Recently,[1-6] advanced theoretical models have been applied to the calculation of the energy and width of the He⁻ $1s2s2p\,^2P^o$ resonance. The calculations presented in the most recent papers[4-6] have used very large wave functions, and the aim was to establish the character of the resonance ("shape" versus "Feshbach"), given the fact that it is quite broad. It was declared[4-6] to be a Feshbach resonance lying between the He $1s2s\,^3S$ and $1s2s\,^1S$ thresholds.

Although it is interesting to see that large wave functions with "correct" projection operators or similar orthogonality constraints yield different results from those computations which employed less carefully chosen wave functions,[1-6] we believe that the really interesting point with this case is that all the theories—in spite of their computational magnitude—have yielded widths which are much smaller than that produced by the recent experiment.[7]

Given the level of sophistication of current scattering theory and experiment, we thought that this resonance constituted a good and timely case for studying and analyzing its localized and continuum components and finding how they affect the observed position and width as *a function of energy*. Applying rigorous resonance theory with accuracy can be a serious computational problem if no previous analysis is made of the nature and electronic structure of the resonance in question. Our approach has been based on previous work[8-11] which

presents such analyses and the results show the following.

(1) The position of the He⁻ $1s2s2p\,^2P^o$ can be found quite accurately with a small (32-term) square-integrable wave function, provided a suitably coupled multiconfigurational Hartree-Fock (MCHF) function is computed and taken as the zeroth-order vector. The "Feshbach" nature of the state is already present in the two-term zeroth-order vector.

(2) The broad resonance is characterized by an *energy-dependent* width. This energy dependence increases the magnitude of the width computed from the standard golden-rule formula, as an energy-independent quantity, bringing it much closer to experiment (see Table I).

II. THEORY

It has been shown[9,10,12] that N-electron resonances can be treated from a many-body point of view by treating the localized part as in ordinary bound states—with some additional constraints. Thus the localized part of a multielectron resonance can be written as $\Psi_0 = \Phi + X$ where Φ is in general a MCHF solution over orbitals of the Fermi sea,[10] and X is the orthogonal to Φ correlation function.[9,10] To a very good approximation, X contains configurations that result from single or double excitations from the orbitals of Φ to those of the virtual space. The virtual orbitals are Slater-type orbitals (STO's) with variationally optimized exponents and are Schmidt orthogonalized to Fermi-sea orbitals and among themselves. Configurations having the same form as the open channels are excluded from the expansion.

TABLE I. Positions and widths of the He⁻ $1s2s2p$ $^2P^o$ resonance.

Source	E (eV)	Γ (meV)
Reference 4 (Theor.)	20.54	
Reference 1 (Theor.)	20.17	330
Reference 2 (Theor.)	20.20	400
Reference 5 (Theor.)	20.52	437
Reference 6 (Theor.)	20.33	355
Reference 7 (Expt.)	20.27	780
Reference 21 (Expt.)	20.30	~1000
This work[a]	20.50	245
This work[b]	20.31	370
This work[c]	20.31	420
This work[d]	20.28	575
This work[e]	20.26	~600

[a]MCHF. The width is evaluated at 20.31 eV in order to compare with calculation b (golden rule).

[b]MCHF plus localized electron correlation plus energy shift due to the open channels (Δ) (golden rule).

[c]Calculation b plus second-order interaction with pseudoresonances [Eq. (11)].

[d]Solution of Eq. (9) in the complex plane.

[e]E_R is the position of the maximum and Γ_R is the full width at half maximum of the theoretical cross section (Fig. 1).

Diagonalization of the Hamiltonian in this basis results in a set of N-electron vectors Ψ_n. We denote Ψ_0 as the one containing Φ with the largest coefficient. The rest are in general pseudoresonances at energies outside the energy region of the true resonance. However, they mix with Ψ_0 through second-order interaction mediated by the open channels. Following Fano[8] we can write the total wave function as

$$\Psi_E = \sum_n a_n(E)\Psi_n + \sum_i \int dE' b_{iE'}(E)u_{iE'} , \qquad (1)$$

where u_{iE} is the wave function of the ith open channel. The vectors Ψ_n are orthogonal to each other but not necessarily to the open channels, since nonorthogonality does not affect the asymptotic form of the total wave function and therefore the scattering parameters. Let us define the matrix element

$$V_{n,iE'}(E) = \langle \psi_n | H - E | u_{iE'} \rangle , \qquad (2)$$

and through it the energy-dependent matrix,[13]

$$F_{mn}(E) = \sum_i \mathscr{P} \int dE' \frac{V_{m,iE'}(E)V_{iE',n}(E)}{E - E'} , \qquad (3)$$

where $\mathscr{P}$ signifies the principal part of the integral. The diagonalization of the matrix $E_n\delta_{mn} + F_{mn}(E)$ gives the second-order mixing of the vectors Ψ_n.

Thus we obtain a new state $\tilde{\Psi}_0$ for the localized part of the resonance at a new energy $E_0 + \Delta(E)$. Both the state and the eigenvalue are slowly varying functions of the energy. We drop the other linear combinations, provided their energies lie outside the region of the resonance. The partial widths $\Gamma_i(E)$ are given by

$$\Gamma_i(E) = 2\pi | \langle \tilde{\Psi}_0 | H - E | u_{iE} \rangle |^2 . \qquad (4)$$

The total width Γ is the sum of the partial ones.

The approximate position of the resonance E_r is given by the solution of the equation

$$E - E_0 - \Delta(E) = 0 . \qquad (5)$$

If $\Delta(E)$ and the $\Gamma_i(E)$'s are slowly varying functions of the energy in the energy region of interest, we can choose their values at the approximate position of the resonance as the ones to be compared with the experiment. Otherwise, it is necessary to plot the cross sections and compare with the experimental ones at every energy point. The cross section is related to the scattering matrix by the formula

$$\sigma_{i \leftarrow j}(E) \sim \frac{1}{k_i^2} \left| \frac{S_{ij}(E) - \delta_{ij}}{2i} \right|^2 , \qquad (6)$$

and we can write $S = S_0^{1/2} S^{res} S_0^{1/2}$, where S_0 is the scattering matrix due to potential scattering only. In the case of an isolated resonance,[14]

$$S_{ij}^{res}(E) = \delta_{ij} - i \frac{\gamma_i(E)\gamma_j(E)}{E - E_0 + i\Gamma(E)/2} , \qquad (7)$$

where $|\gamma_i|^2 = \Gamma_i$. Owing to the nature of the excitation ($1s \rightarrow 2s$) and the smallness of the corresponding R^k integrals, the effect of the direct mixing of the open channels $1s^2\epsilon p$ and $1s2s\,^3S\epsilon p$ on the cross section is expected to be negligible compared to their indirect mixing through the resonance. Therefore the matrix S_0 is almost diagonal, and the inelastic cross section is not affected by its presence. So, we have

$$\sigma_{in}(E) \sim \frac{1}{k_0^2} \frac{\Gamma_0(E)\Gamma_1(E)/4}{[E - E_0 - \Delta(E)]^2 + \Gamma^2(E)/4} , \qquad (8)$$

where the index 0 refers to the elastic and the index 1 to the inelastic channel. It appears then that we cannot talk about energy-independent position or width of the resonance. Nevertheless, theories treating resonances as decaying states define such a pair of energy-independent qualities. These are given by the solution of the equation[10]

$$Z - E_0 - \Delta(Z) + i\Gamma(Z)/2 = 0 \qquad (9)$$

in the complex plane. A meaningful connection between the two approaches can then be made by

transferring the energy dependence of the quantities Δ and Γ to a modified potential scattering matrix S_0. In the single-channel case this is easily done by a least-squares fit of the cross section. When more than one channel is open, such a deconvolution appears to be complicated.

In this work, in order to have a more rigorous comparison with experiment, we have (1) computed the inelastic cross section and compared it directly to the experimental one (Fig. 1) and (2) extracted a position E_R and a width Γ_R of the resonance by going beyond the standard golden-rule formula and solving Eq. (9) to a good approximation.

III. COMPUTATION OF Ψ_0: A TWO-TERM MULTICONFIGURATIONAL HARTREE-FOCK FUNCTION PREDICTS A FESHBACH RESONANCE

As in every many-electron treatment of many-electron states, the choice of the zeroth-order vector is crucial to the qualitative description of the corresponding state as well as to the rate of convergence to the exact answers. A few years ago, using the virial theorem as a guiding principle for localization and convergence to the necessary local minimum, as well as suitable cutting-off procedures, analytic Hartree-Fock (HF) theory was applied to the calculation of the zeroth-order vectors of highly excited
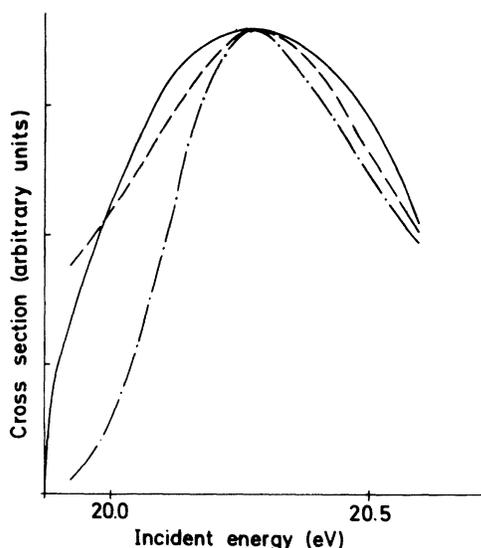
FIG. 1. Inelastic cross section of He at incident energies between the 2^3S and 2^1S thresholds. Experimental cross section of Brunt et al. (Ref. 7) (solid curve). Lorentzian distribution with the same maximum and width as the experimental cross section (dashed curve). Theoretical cross section calibrated to the same height as the experimental one (dot-dashed curve).

autoionizing states.[9] This approach, although it is of course basis-set dependent and often difficult in yielding convergence, has the advantage of producing good zeroth-order descriptions of even diffuse resonances. (Negative ions may sometimes be characterized by positive orbital eigenvalues.)

Numerical HF theory[15] bypasses the basis-set problem. Using suitable extrapolation techniques based on noninteger nuclear charges and noninteger electron occupations in the calculation of the required integrals, we and Beck have demonstrated (Refs. 10, 11, 16, and this work) that numerical HF and MCHF solutions can be obtained for a number of valence excited resonances (HF functions for inner-hole excited states are relatively easy to compute[17]).

For the state of interest, a two-configuration ($1s2s2p\ ^3P$ and $1s^22p$) MCHF solution was chosen as the zeroth-order function. The solution is found by choosing the vector with the largest coefficient in front of $1s2s2p\ ^3P$. It is of the form

$$\Phi = 0.995 \mid 1s\,2s\,2p\ ^3P \rangle$$
$$-0.099 \mid 1s^22p \rangle \tag{10}$$

and gives an energy of -2.1503 a.u. This eigenvalue is *below* the energy of the He $1s2s\ ^1S$ threshold which lies at $-2.145\,97$ a.u.[18]

In computing Φ and later X, we chose the coupling to be in the $n=2$ shell, where the interactions are greatest. The more common[1-6] coupling between the $1s$ and $2s$ electrons, $1s2s\ ^{3,1}S\,2p$, is less desirable for computational reasons. On the other hand, in order to establish correspondence between the physics of the scattering experiment and the $n=2$ coupling, one can develop the $1s2s2p\ ^3P$ configuration as a linear combination of $1s2s\ ^1S\,2p$ and $1s2s\ ^3S\,2p$ with coefficients $\sqrt{3}/2$ and $-\frac{1}{2}$, respectively. The presence of the $1s^22p$ component prevents an energy collapse and allows for a proper convergence, in analogy with the better-known case of the HF solution for the $1s2s\ ^1S$ state.[15]

By analyzing the zeroth-order wave function in this way, we observe that it contains a large part associated with the closed channel $1s2s\ ^1S\,\epsilon p$ and two smaller parts that can be expanded in terms of the wave functions of the open channels $1s2s\ ^3S\,\epsilon p$ and $1s^2\epsilon p$. So, we have absorbed part of the open channels into the localized part Φ of the resonance and, in doing so, we included part of the energy shift Δ into E_0.

Thus we have demonstrated that a two-term, properly optimized wave function resolves the question of "shape versus Feshbach" resonance for the He$^- 1s2s2p\ ^2P^o$ state,[1-6] *as its energy is below the $1s2s\ ^1S$ threshold and its main component represents*

a closed channel. However, we note that such a statement can be made rigorously only because the experimental position of the resonance is available. Otherwise, such a conclusion can be drawn only at the end of the calculation, after the energy shift due to the correlation function X, which is always negative, and the energy shifts due to the open channels, *which can have either sign,* have been computed. This comment applies as well to the work presented in Refs. 4 and 5, where the effect of the open channels was neglected.

IV. INCLUSION OF CORRELATION AND NONORTHONORMALITY

The main contribution to the correction X, and therefore to the energy, comes from the single excitations $2s \rightarrow V_d$ as well as from the double excitations $2s2p \rightarrow V_s V_p$ and $2s2p \rightarrow V_p V_d$, where V_l are virtual orbitals. Other single excitations such as $2s \rightarrow V_s$ and $2p \rightarrow V_p$ and double ones such as $2s2p \rightarrow V_d V_f$ are also included, although their contribution is much smaller. Configurations of the form $1s2s \, ^3S \, V_p$ and $1s^2 V_p$, which are similar to the open channels, are excluded from the expansion. The final wave function contains 32 configurations constructed from the three HF orbitals and 11 virtual orbitals. It gives an energy $E_0 = -2.1585$ a.u. This is very close to the experimental position of the resonance which is 20.27 eV above the ground state of He, that is, $E_r^{\text{expt}} = -2.1587$ a.u.[7]

As with the calculation of radiative transition processes with separately optimized HF and correlation functions for the initial and final states,[10,19] the correct treatment of resonance widths, in theories which calculate them from transition matrix elements, requires the inclusion of *nonorthonormality* effects between zeroth-order scattering and resonant wave functions. The recent calculation of core-excited shape resonances in He^- was based on such a formulation.[11] This possibility was taken into account in the formulas written above, by using the operator H-E instead of simply H.

In our case, the open channels with the correct symmetry are the $1s^2 \epsilon p$ and $1s2s \, ^3S \, \epsilon p$, where the He atom is in its ground and first excited states, respectively. We use HF solutions for the core orbitals and fixed-core HF solutions for the zeroth-order scattering orbitals.

V. RESULTS AND DISCUSSION

Neglecting the $1s^2 \epsilon p$ continuum whose contribution to the total width is negligible[5,6] as well as the coupling to the pseudoresonances, we find, by applying formulas (2)–(5), $\Delta = 0.0013$ a.u. and $\Gamma = 370$ meV. In order to improve this value, we included in

the expansion (1) the pseudostates arising from the diagonalization of the Hamiltonian in the space of square-integrable functions. There are 30 such states in our calculation at energies above the $1s2s \, ^1S$ threshold and one at an energy well below the $1s2s \, ^3S$ threshold. The latter one represents the pseudostate where the $1s \, ^2 2p$ configuration is dominant. We observe that the energy region of our interest, between the two thresholds, is clear from pseudoresonances. As was discussed above, the pseudostates have a second-order interaction with Ψ_0, modifying in this way the resonance width, which is now energy dependent and is given by

$$\Gamma(E) = 2\pi \left| \sum_{n=0}^{N} V_{nE}(E) A_n(E) \right|^2 , \qquad (11)$$

where $A_n(E)$ are the mixing coefficients resulting from the diagonalization of $E_n \delta_{mn} + F_{mn}(E)$. Instead of diagonalizing this matrix, for many values of the energy, we make use of the smallness of the quantities F_{mn} and apply first-order perturbation theory to obtain

$$A_n(E) = \frac{F_{n0}(E)}{E_0 - E_n} A_0(E) , \qquad (12)$$

where A_0 is given by the condition $\sum |A_n|^2 = 1$. The value of A_0 is found to be close to unity in the energy region of interest. The approximate position of the resonance E_r is given by the solution of Eq. (5), where

$$\Delta(E) = F_{00}(E) + \sum_{n=1}^{N} \frac{|F_{n0}(E)|^2}{E - E_n} . \qquad (13)$$

Because of the smallness of the quantities F_{n0}, the last term does not contribute significantly to the energy shift, which retains the value given above. The width is now given by the formula

$$\Gamma(E)$$
$$= 2\pi A_0^2 \left| V_{0E}(E) + \sum_{n=1}^{N} V_{nE}(E) \frac{F_{n0}(E)}{E_r - E_n} \right|^2 . \qquad (14)$$

This formula takes into account the interaction of Ψ_0 with the continuum through the closed channels. The resulting value of the width is 420 meV, in agreement with other calculations (Table I) but still far away from the experimental value. However, the identification of $\Gamma(E_r)$ as the width of the resonance is based on the assumption of constancy of the quantities Γ and Δ in the energy region of the resonance. We found that this assumption is wrong in our case, being correct only for the small partial width due to the $1s^2 \epsilon p$ channel. The plot of the inelastic cross section (Fig. 1), calibrated to the same

height at the maximum as the experimental one, gives an apparent "width" of approximately 600 meV and a position of the peak at -2.1592 a.u. However, because of its significant departure from the Lorentzian shape neither can be taken to correspond to the standard definitions of resonance position and width. The same comment applies to the experimental cross section.

Finally, we look at Eq. (9) which defines the position of the resonance in the complex plane. This equation was derived in Ref. 10, where a time-dependent point of view was presented. Questions of analytic continuation and connections to other theories were also discussed. The complex energy position can also be derived by employing Fano's theory and outgoing boundary conditions on resonance.[12]

The same equation has been derived and illustrated on a simple model by Drachman[20] for the case of elastic scattering. By making, as he did, a Taylor expansion of Γ and Δ about the approximate position E_R and retaining linear terms, we obtain

$$E_R - E_r = -\frac{1}{4}\frac{\Gamma_r'}{1-\Delta_r'}\Gamma_R$$

and

$$\Gamma_R = \frac{\Gamma_r}{1-\Delta_r'} + \frac{\Gamma_r'}{1-\Delta_r'}(E_R - E_r) \; ,$$

where the quantities with subscript r are evaluated at $E = E_r$. In our case $\Gamma_r' = 0.4514$ and $\Delta_r' = 0.3475$. Therefore we obtain

$$E_R = -2.1583 \text{ a.u.}$$

and

$$\Gamma_R = 575 \text{ meV} \; .$$

We observe that these values are quite close to the ones obtained from the plot of the cross section.

The results of our computations are collected in Table I together with the results of other theories and experiments. Approximations (a)—(e) constitute a hierarchy which demonstrates the magnitudes and trends of the various approaches for this resonance. For example, we observe that our two-term MCHF calculation already yields a better energy than the calculations of Refs. 4 and 5 where 54 and 40 configurations were employed, respectively.

We close by pointing out the conceptual similarity of the "saddle-point technique" of Ref. 4 to the analysis and approach to the variational calculation of inner-hole excited states presented earlier in Ref. 9, where emphasis was put on the importance of orthogonality constraints of the trial functions to

zeroth-order core orbitals. The form of the $q = 1 - |nl\rangle\langle nl|$ projection operator of Ref. 9 (p. 2088) is the same as the one of Ref. 4. The choice of the orbital $|nl\rangle$ is different. In Ref. 4 it is hydrogenic, whose nonlinear parameter is optimized by maximizing the total E. However, given the reality of the many-body problem, the purported relationship of this technique to the rigorous establishment of resonances[4,22] is unclear.

VI. SYNOPSIS

Many-electron autoionizing states giving rise to resonance phenomena present interesting and fundamental problems as regards the accurate description of their electronic structure and the rigorous definition and computation of the observed quantities: the position and the width.

In this paper we have studied the $He^- 1s2s2p\ {}^2P^o$ state. Our interest in it arose from the fact that, in spite of the apparent rigor and computational magnitude of recent theories,[4-6] a serious discrepancy between experiment and theory appeared as regards the *width* of the resonance. We note that the physical significance of this fact was not emphasized by the previous groups, who aimed at establishing whether this resonance is a closed-channel resonance or not.[4]

The basic aspects of our theory are the following.

(1) The zeroth-order localized part of the resonance is described by a two-term MCHF function [Eq. (10)]. The question of Feshbach versus shape resonance is already resolved at this stage. Electron correlation is included variationally. Questions about lower states and open channels are answered within the framework of the theory of Refs. 9 and 10.

(2) The standard golden-rule-type formula for the calculation of widths is improved by including second-order effects due to the N-electron pseudo-states Ψ_n [Eq. (11)]. Nonorthonormality effects between initial- and final-state configurations are included explicitly by redefining the interaction matrix elements [Eq. (2)].

(3) Having developed accurate methods for obtaining $\Gamma(E)$ and $\Delta(E)$ as functions of energy, the energy dependence of this broad resonance is demonstrated via the approximate solution of the defining Eq. (9) in the complex energy plane and via the calculation of the inelastic cross section [Eq. (6)]. The second procedure provides a direct comparison with experiment. The first is mainly of theoretical interest and can be compared with the experimental values only when the elastic and all the inelastic cross sections are known accurately. In this case, a least-squares fitting could determine the

values of E_R and Γ_R as well as the partial widths.

Both of these calculations improve the agreement with experiment. However, some discrepancy remains. On the theoretical side, a further but small improvement might occur via sizable increase of the number of configurations describing the diffuse function $\tilde{\Psi}_0$.

Finally, given the discrepancy between the result of the large (126 configurations) complex coordinate calculation[6] and experiment (Table I), we suggest that more applications of this method to *broad* resonances should be made in order to establish the range of its flexibility or validity.

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