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P Auto-Ionization States of He and H$^-$

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Precision calculations of the energies of P auto-ionization states of He and H$^-$ are continued, and calculations of widths and shifts are initiated. The P-wave Hylleraas-type wave function of a previous calculation (Bhatia, Temkin, and Perkins) is augmented to include 56 terms, among them the most important powers of r_1, r_2, and r_{12} omitted in the previous calculation. The associated wave functions are then used to calculate shifts, widths, and q values with exchange, exchange adiabatic, and polarized orbital wave functions representing the nonresonant continuum. It is found that the latter gives the most satisfactory agreement with experiment. Corrections for nearby resonances are also included. The variational calculation has been extended to include 84 terms for the ^1P states of He. With inclusion of the shift, the positions of the first two resonances are within the experimental values of Madden and Codling; however, the lowest state is about 0.01 eV removed from the central value of the experiment. The mass-polarization correction is also discussed, but its value is far too small to reconcile the deviation from the mean.

I. INTRODUCTION

The auto-ionization states of an N-electron atomic system lie in the continuous spectrum of scattering states of an electron from the N-1 electron system. Thus they do not correspond to stationary state solutions of the N-electron Hamiltonian,[1] and they may auto-ionize by electron emission leaving behind bound states of the N-1 electron system. If the auto-ionization states live long enough, however, they may alternatively decay by radiation to truly bound states of the N-electron system. Because the coupling to the radiation field is relatively weak, one may use this radiation as a probe of the auto-ionization states predicted by the Schrödinger equation. One significant aspect of this circumstance, which underlies the calculations in this paper, is the fact that radiative processes, being susceptible to orders of magnitude greater experimental precision than ordinary electron scattering parameters, provide a means of experimentally testing what are ultimately continuum solutions of the Schrödinger equation to much greater accuracy than has heretofore been possible.

A prime example of such radiatively accessible auto-ionization states are the ^1P (odd-parity) series of He observed in vacuum ultraviolet absorption by Madden and Codling.[2] For He, being a two-electron system, is simple enough to enable one to carry out quantitative calculations of high precision; in addition the N-1 system (He+), is a one-electron system, so that one can construct a satisfactory Q operator of the Feshbach theory[3] explicitly[4] and thus convert the essential part of the resonance problem to an eigenvalue problem which can be solved variationally in complete analogy with bound-state calculations.[5]

In a previous calculation a Hylleraas variational form was introduced and the nontrivial problem of the Q projecting with such a wave function was solved.[6] The results were sufficiently lower and convergent looking as compared with previous calculations to give some confidence that, as in the low-lying bound states, such a wave function could be used as the basis of precision calculations. However, in our original paper we inadvertently omitted the most important triples of powers of r_1, r_2, and r_{12} from the P-state part of our calculation; therefore optimum P-wave results were not forthcoming at that time. Interim reports[7] gave initial results with the additional terms included. In the present paper that calculation is concluded as follows: Energy positions of the first three ^1P states and the first four ^3P states of He and their associated widths are calculated. Also the position, width, and energy shift of the lowest ^3P state of H$^-$ is calculated because of its experimental observability in electron-hydrogen scattering. For the lowest triplet and all three singlet P states of He we have also computed the energy shifts and q values again in order to compare with experiment.

Widths and shifts within the Q-operator formalism require a knowledge of the nonresonant scattering wave function. Although a formal equation can be written down for this function,[5] it involves an infinite series of nonlocal potential terms with a continuum superposed. The most important discrete terms can be and have been included but the presence of the continuum poses a nontrivial problem. In fact it is likely that an exhaustive solution of this problem would be at best as difficult as a comparable solution of the complete scattering problem. One of the major potential items of usefulness of the Q-operator formalism is that one should not have to know the nonresonant continuum function to the same degree of accuracy as the resonant function in order to get results of the accuracy inherent in the resonant part of the wave function. Because of the uncertainty in the present experimental results, it is perhaps the examination of which continuum functions give the most satisfactory agreement with experiment which yields the most concrete conclusions of this investigation. With regard to our ultimate aim of providing a precision check of the Schrödinger equation in its continuous spectrum, it would appear that the energy positions themselves provide the presently most rigorous test. The last nonrelativistic correction required to effect this comparison is the mass polarization, which we consider in Sec. V. We point out that this correction is not trivially calculated in the Q-operator formalism, nevertheless for the accuracy required we argue that the naive expression should certainly be adequate. The expression is evaluated and found to be very small and insufficient to explain a persistent 0.01-eV discrepancy from the experimental results in the lowest ${}^1P$ auto-ionization line.

II. EIGENVALUES OF H_{QQ}

The most general P-wave function can be written[7, 8]

$$\Phi(\vec{r}_1,\vec{r}_2) = -\cos(\tfrac{1}{2}\vartheta_{12})(f\pm\tilde{f}\,)\,\mathcal{D}_1^{1+}(\theta,\phi,\psi)$$
$$-\sin(\tfrac{1}{2}\vartheta_{12})(f\mp\tilde{f}\,)\,\mathcal{D}_1^{1-}(\theta,\phi,\psi), \qquad (2.1)$$

where the $\mathcal{D}$ are the rotational harmonics, depending on symmetric Euler angles θ, ϕ, ψ.[8] The trial wave function is said to be of the Hylleraas-type when the radial functions, $f=f(r_1,r_2,r_{12})$, are written as positive power expansions in terms of r_1, r_2, r_{12}, namely,

$$f = e^{-\gamma(r_1+r_2)}$$
$$\times \sum_{l\geqslant 1}\ \sum_{m\geqslant 0}\ \sum_{n\geqslant 0} C_{lmn}\, r_1^{\,l}\, r_2^{\,m}\, r_{12}^{\,n}\ . \qquad (2.2a)$$

In Eq. (2.1) it is understood that

$$\tilde{f}\,(r_1,r_2,r_{12}) \equiv f(r_2,r_1,r_{12}), \qquad (2.2b)$$

and the upper (lower) sign in Eq. (2.1) refers to the singlet (triplet) state.

It is of interest to compare Eq. (2.2a) with the choice of terms that was inadvertently made in BTP.[6] There we had $m\geqslant 1$ and $l\geqslant 0$ in place of the summation limits in Eq. (2.2a). Including only one term of Eq. (2.2a) in Eq. (2.1), we presently have

$$\Phi \propto e^{-\gamma(r_1+r_2)}[\cos(\tfrac{1}{2}\vartheta_{12})(r_1\pm r_2)\,\mathcal{D}_1^{1+}$$
$$+\sin(\tfrac{1}{2}\vartheta_{12})(r_1\mp r_2)\,\mathcal{D}_1^{1+}\,]\ . \qquad (2.3a)$$

Using the explicit form of $\mathcal{D}_1^{1\pm}$ and the connection between our Euler angles and spherical angles of $\vec{r}_1$ and $\vec{r}_2$,[8] we find (for $\gamma = 1$)

$$\Phi \propto R_{2s}(r_1)R_{2p}(r_2)\,Y_{10}(\Omega_2) \pm (1 \rightleftarrows 2)\ . \qquad (2.4a)$$

This is the explicit form of a $(2s2p)$ wave function which is well known to be the dominant configuration of the lowest doubly excited P state. On the other hand, with the choice in BTP the lowest term corresponds to

$$\Phi \propto e^{-\gamma(r_1+r_2)}[\cos(\tfrac{1}{2}\vartheta_{12})(r_1\pm r_2)\,\mathcal{D}_1^{1+}$$
$$-\sin(\tfrac{1}{2}\vartheta_{12})(r_1\mp r_2)\,\mathcal{D}_1^{1-}]\ . \qquad (2.3b)$$

The difference between Eqs. (2.3a) and (2.3b) is simply the opposite sign of the second term. However, on rewriting Eq. (2.3b) in spherical coordinates we find

$$\Phi \propto R_{2s}(r_1)\,Y_{10}(\Omega_1)R_{2p}(r_2) \pm (1 \rightleftarrows 2). \qquad (2.4b)$$

In this form it is seen that the angular factor is now associated with the $2s$ radial function and thus has no obvious physical significance. It is not surprising therefore that Eq. (2.2a) leads to improved results (and convergence), but it is interesting to note that Eq. (2.4b) is a completely acceptable ansatz from the mathematical point of view.

The alteration of the wave function causes no difficulty in the formal evaluation of the Q projection.[6] Specifically the term $\langle\Phi HP_1\Phi\rangle$ becomes

$$\langle\Phi HP_1\Phi\rangle \propto \int\!\!\int d^3r_1 d^3r_2\,\Phi(\vec{r}_1,\vec{r}_2)H$$
$$\times\varphi_0(r_1)Y_{l0}(\Omega_2)F_l(r_2)/r_2\ , \qquad (\text{A}.10')$$

where

$$F_l(r_2) = \int\!\!\int r_1 dr_1\, r_{12} dr_{12}\, \varphi_0(r_1)$$
$$\times[\cos\vartheta_{12}(f\pm\tilde{f}\,)]\ . \qquad (\text{A}.8')$$

The function in square brackets in (A.8′) is reminiscent of the radial functions as they arise in Breit's form of the odd-parity P-wave function.[9] In fact it follows from Eq. (2.1) and Appendix III of Ref. 8 that they are essentially the same.

The actual calculation requires the evaluation of

$$\mathcal{E}_Q = \langle \Phi Q H Q \Phi \rangle / \langle \Phi Q \Phi \rangle \ . \tag{2.5}$$

The definition of Q and the decomposition of the right-hand side of Eq. (2.5) are given in BTP. For f given by Eq. (2.2a) one encounters one new type of integral over what was needed there. The integrals in question are of the form

$$I(L,M,N;\ a,b) \equiv \iiint e^{-(ar_1+br_2)} \times r_1^{\,L} r_2^{\,M} r_{12}^{\,N} r_1 dr_1 r_2 r_{12} dr_{12} \ ,$$

where now M can be as negative as -4. Although the various integrals can lead individually to exponential integrals involving a and b, they can always be recombined such that the noncancelling terms reduce to a form containing at most a transcendental factor

$$\ln[(a+b')/(a+b)] \ ,$$

which is readily evaluated by the machine IBM 360-91.

In Table I we present results as functions of the Pekeris numbers[10] for P states, i.e., the number of terms

$$N(\omega_i) = \sum_{\omega_i=1}^{\omega} n(\omega_i),$$

where $n(\omega_i)$ contains all terms $r_1^{\,l} r_2^{\,m} r_{12}^{\,n}$ such that $l+m+n=\omega_i=1,2,\ldots,7$. For example $N(7)=84$. In each case the nonlinear parameter given has been optimized for the 56-term expansion corresponding to the state in question. The entries for the lowest singlet and triplet states of He represent typographical corrections to previously given results.[7] The apparent convergence is obvious from the table, however in view of the lack of knowledge of the extent of long-range potentials in the variational problem associated with H_{QQ} we have refrained from making any extrapolations.

In Table II we have collected our lowest results and compared them with previous calculations using the same Q operator. The results include a reduced mass correction; effectively this amounts to multiplying the Rydberg for infinite mass by a reduced mass factor which is given in the caption of the table for both He and H$^-$. The He results for the two lowest states of each symmetry given are seen to be the lowest calculated. However, the ^1P results for H$^-$ are blatantly absent; not only have we not calculated values lower than the two reported by O'Malley and Geltman,[5] but we have found no auto-ionization states in this symmetry at all. This indicates that these states must be of enormous size[11]; however, we know that they must exist in the nonrelativistic approximation.[11, 12] The reason that some eigenvalues do occur in Ref. 5, for example, is because the trial functions contain a sufficient number of exponential parameters which can become small enough to allow for the requisite range.

The only nonrelativistic corrections that remain are in the shift and the mass polarization. These are discussed in two of the succeeding sections.

III. WIDTHS, SHIFTS, THE NONRESONANT CONTINUUM

The position of a resonance is usually defined theoretically as that energy at which the phase shift attains the value of $\frac{1}{2}\pi$ plus its preresonant value.[13] This point can be written[5]

$$E = \mathcal{E}_Q + \Delta_Q, \tag{3.1}$$

where Δ_Q represents the shift of the eigenvalues computed in the last section. The definition makes it clear that one is dealing with a scattering phenomenon, nevertheless if the coupling of the auto-ionization state to the continuum is weak, one can expect to deal with this aspect of the prob-

TABLE I. $\mathcal{E}_Q$ (in Ry) versus the number of terms N in the Hylleraas expansion.

	He							H$^-$
	^1P			^3P				^3P
$N(\omega)$	$-\mathcal{E}_1$ $\gamma=0.85$	$-\mathcal{E}_2$ $\gamma=0.65$	$-\mathcal{E}_3$ $\gamma=0.60$	$-\mathcal{E}_1$ $\gamma=0.95$	$-\mathcal{E}_2$ $\gamma=0.60$	$-\mathcal{E}_3$ $\gamma=0.60$	$-\mathcal{E}_4$ $\gamma=0.55$	$-\mathcal{E}_1$ $\gamma=0.40$
10(3)	1.380 936	1.169 403	1.021 734	1.520 980	1.125 315	1.071 363	0.993 597	0.283 064
20(4)	1.385 634	1.173 689	1.099 652	1.522 924	1.157 320	1.127 209	1.072 777	0.285 077
35(5)	1.385 739	1.193 095	1.107 076	1.522 968	1.160 317	1.154 845	1.089 824	0.285 139
56(6)	1.385 781	1.193 341	1.125 733	1.522 980	1.169 163	1.156 144	1.095 434	0.285 194
84(7)	1.385 789 5	1.194 170 7[a]	1.126 398 5	...	...	...	...	...

[a] We have noticed the peculiar convergence pattern engendered by this result; however, it is not a typographical mistake.

TABLE II. Comparison of $\mathcal{E}_Q$ in eV with other calculations. These results include a reduced mass correction in converting to eV. This implies an effective rydberg of 13.603 50 eV for He, and of 13.579 40 eV for H^-. In helium the energies are given relative to the ground state of He, whereas in H^- the energies are relative to the ground state of H.

System	n	Present	BTP (Ref. 6)	OG (Ref. 5)	AM[a]
He (^1P)	1	60.1500	60.192	60.186	60.340
	2	62.7567	•••	62.777	62.791
	3	63.6787	•••	63.712	63.707
He (^3P)	1	58.284	58.289	58.300	58.41
	2	63.097	•••	63.145	63.18
	3	63.274	•••	63.931	63.29
	4	64.100	•••	64.123	64.12
$H^-(^3P)$	1	9.707	9.712	9.709	•••

[a] P. Altick and N. Moore: singlet results from Phys. Rev. 147, 59 (1966) and triplet results from Phys. Rev. Letters 15, 100 (1965).

lem in some kind of perturbation theory. Under the usual assumption of a one pole approximation, i.e., an isolated resonance, an exact formula for Δ_Q can be written as follows[13]:

$$\Delta_Q = \frac{1}{2\pi}\, \mathcal{P}\int_0^\infty \frac{\Gamma(E')}{\mathcal{E}-E'}\, dE' , \tag{3.2}$$

where $\mathcal{P}$ signifies the principal value. In the vicinity of a particular resonance n, the width formula is[5]

$$\Gamma_n(E) = 2k\,|\langle P\Upsilon_n | H | Q\Phi_n\rangle|^2 . \tag{3.3}$$

In these formulas rydberg units have been used throughout. The width of the nth resonance is defined as Γ_n:

$$\Gamma_n \equiv \Gamma_n(E_n) . \tag{3.4}$$

$Q\Phi_n$ is the exact eigenfunction of the projected problem, which we have discussed in the previous section, and E_n is the total energy at the nth resonance. Writing the Hamiltonian in the form

$$H = H_0 + 2/r_{12} , \tag{3.5}$$

and noting that P and Q commute with H_0 and that $PQ=0$, one can reduce Γ_n to the much simpler computational form[14]

$$\Gamma_n(E) = 2k\,|\langle P\Upsilon_n(E) | (2/r_{12}) | Q\Phi\rangle|^2 . \tag{3.6}$$

$P\Upsilon_n(E)$ is the solution of the optical potential problem less the resonant term[5]:

$$(H' - E)P\Upsilon_n = 0, \tag{3.7}$$

where
$$H' = H_{PP} + \mathcal{V} . \tag{3.8a}$$

$$\mathcal{V} = \sum_{j(\neq n)} \frac{H_{PQ}|\Phi_j\rangle\langle\Phi_j|H_{PQ}}{E_n - \mathcal{E}_j} . \tag{3.8b}$$

H_{PP} is the exchange approximate Hamiltonian; it has a well-known solution of the form[15]

$$\Psi^{(\mathrm{ex})} = P\Psi^{(\mathrm{ex})} = \frac{1}{\sqrt{2}}\left[\frac{u_l(r_1)}{r_1} Y_{l0}(\Omega_1)\, \varphi_0(\vec{r}_2) \pm (1 \rightleftarrows 2)\right] \tag{3.9}$$

with
$$\varphi_0(\vec{r}) = 2Z^{\frac{3}{2}} e^{-Zr} Y_{00}(\Omega) . \tag{3.10}$$

The function $u_l(r)/r$ is normalized as a plane wave or its Coulomb counterpart:

$$\lim_{r\to\infty} u_l(r) = \frac{\sin(kr + \sigma_l - \frac{1}{2} l\pi + \eta_l)}{k} , \tag{3.11}$$

where σ_l is the Coulomb phase factor[16]:

$$\sigma_l = (1 - \delta_{\zeta 0}) \arg[\Gamma(l+1-i\zeta/k)] + \frac{\zeta}{k} \ln 2kr , \tag{3.12}$$

and ζ is the net charge on the target system ($\zeta = Z - 1$, where Z is the charge on the nucleus).

For the cases at hand ζ is 1 and 0 for He and H^-, respectively. The quantity η_l is the residual phase shift. Since we are dealing with P states, we have $l = 1$ in all of the present calculations. The energy of the scattered particle is k^2, and it is related to the total energy E by

$$E = E_t + k^2 , \tag{3.13}$$

where E_t is the ground-state energy of the target system (He^+ and H, respectively).

$P\Upsilon_n(E)$ has the same asymptotic form as $\Psi^{(\mathrm{ex})}(E)$. This means, then, that in our plane-wave normalization

$$\int \chi(E_1)\, \chi^*(E_2)\, d^3r_1\, d^3r_2 = (\pi/k_1)\, \delta(k_1^2 - k_2^2) , \tag{3.14}$$

where χ is either $P\Upsilon$ or $\Psi^{(\mathrm{ex})}$.

We now come to the important question of calculating $P\Upsilon$. It is clear that $\Psi^{(\mathrm{ex})}$ constitutes the zeroth-order approximation to it. The correction terms come from the additional potential $\mathcal{V}$ defined in Eq. (3.8a). It is essential to recognize that this sum in fact contains an integration over continuum functions of Φ; for which $\mathcal{E}_j$ is greater than (or equal to) the first excited state of the target. The discrete terms in $\mathcal{V}$ present no particular problem in that a perturbation theory can readily be constructed and rapid convergence can confidently be expected. Letting $\delta\Psi$ be the increment to $\Psi^{(\mathrm{ex})}$ coming from $\mathcal{V}$, and using an integral representation for it:

$$\delta\Psi(E)=\int_{E'\neq E} f(E')\Psi^{(\mathrm{ex})}(E')\,dE' , \tag{3.15a}$$

we can readily solve for $f(E')$ with the help of Eq. (3.14) and rewrite Eq. (3.15a) explicitly in the form

$$\delta\Psi(E)=\frac{\mathcal{P}}{\pi}\int dE'\,\frac{k'\Psi^{(\mathrm{ex})}(E')}{E-E'} \times\langle\Psi^{(\mathrm{ex})}(E')|\mathcal{V}|\Psi^{(\mathrm{ex})}(E)\rangle . \tag{3.15b}$$

The increment to the matrix element involved in Γ then becomes

$$\delta V\equiv\langle\delta\Psi(E_n)|H_{PQ}|\Phi_n\rangle = \frac{1}{\pi}\sum_{j(\neq n)}\frac{\langle\Phi_j|H_{QP}|\Psi^{(\mathrm{ex})}(E_n)\rangle}{E_n-\mathcal{E}_j}\,\mathcal{P}\int dE'k' \times\frac{\langle\Psi^{(\mathrm{ex})}(E')|H_{PQ}|\Phi_n\rangle\langle\Psi^{(\mathrm{ex})}(E')|H_{PQ}|\Phi_j\rangle}{E_n-E'} . \tag{3.16}$$

The integration over E' for the discrete terms can be handled just as it is in the evaluation of Δ_Q.

The continuum part of $\mathcal{V}$ presents a much more difficult problem. Physically it is by now well known that the major part of the nonresonant corrections to the exchange-approximation phase shifts come from the polarizability of the target.[17] Whereas this distortion of the atom can be described by a superposition of discrete as well as continuum states,[18] in the manner in which they are incorporated in the method of polarized orbitals,[17,19] the phase shifts exhibit a strictly nonresonant behavior. Furthermore the nonresonant photodetachment cross sections for H⁻ and He as computed in this approximation by Bell and Kingston[20] (in the length formulation) agree remarkably well with experiment. Accordingly we shall assume that continuum contributions of $\mathcal{V}$ can be largely included by replacing $\Psi^{(\mathrm{ex})}$ by its polarized orbital extension $\Psi^{(\mathrm{pol})}$:

$$\Upsilon\rightarrow\Psi_l^{(\mathrm{pol})}=[u_l(r_1)/r_1]\,Y_{l0}(\Omega_1) \times[\varphi_0(r_2)+\varphi^{(\mathrm{pol})}(r_1;r_2)]\pm(1\rightleftharpoons 2) , \tag{3.18a}$$

where

$$\varphi^{(\mathrm{pol})}=-[\epsilon(r_1r_2)/r_1^2] \times\frac{e^{-Zr_2}(\frac{1}{2}Zr_2^2+r_2)}{\sqrt{Z}}\,\frac{\cos\vartheta_{12}}{\sqrt{\pi}} \tag{3.18b}$$

and $\epsilon(r_1r_2)$ is a step function.[18]

It is important to realize that in all matrix elements with which we shall be concerned the continuum wave function must be operated on P, and that (unlike $\Psi^{(\mathrm{ex})}$) for $l=1$,

$$P\Upsilon\rightarrow P\Psi^{(\mathrm{pol})}\neq\Psi^{(\mathrm{pol})} .$$

IV. RESULTS, COMPARISON WITH EXPERIMENT

The width including all the corrections mentioned previously may be written

$$\Gamma=2k|V_1+V_2|^2+\delta\Gamma . \tag{4.1}$$

V_1 is the matrix element coming from the exchange-like part of the continuum function. In the exchange approximation this includes the whole function Eq. (3.9), whereas in the polarized orbital approximation it comes from the unpolarized part of Eq. (3.18) (i.e., the terms not containing $\varphi^{(\mathrm{pol})}$. Differences in the values of V_1 therefore come only from differences in the scattered radial function, $u_1(r)$, in different approximations.

The quantity V_2 is the part of the matrix element coming from $\varphi^{(\mathrm{pol})}$. It is present only in exchange-adiabatic and polarized orbital approximations. $\delta\Gamma$ is the correction due to other resonances. It may be calculated implicitly from Eq. (3.16), Eq. (4.1), and the formula

$$\Gamma=2k|V_1+V_2+\delta V|^2 . \tag{4.2}$$

This correction is very small; it comes predominantly from only the one term in the j sum in Eq. (3.16) corresponding to the "wide" resonance in closest proximity to the resonance in question. To the accuracy required it is sufficient to evaluate δV using continuum functions of the exchange approximation.

Finally we compute q values. According to Fano[13]

$$q_n=\frac{\langle Q\Phi_n|T|\Psi_i\rangle}{kV(E_n)\langle P\Upsilon_n(E_n)|T|\Psi_i\rangle}+\delta q_n , \tag{4.3}$$

where

$$\delta q_n=\frac{1}{\pi}\mathcal{P}\int dE'V(E')\,\frac{\langle P\Upsilon_n(E')|T|\Psi_i\rangle k'}{E_n-E'} \times[kV(E_n)\langle P\Upsilon_n(E_n)|T|\Psi_i\rangle]^{-1} \tag{4.4}$$

$$\text{and} \quad V(E) = V_1 + V_2 \,, \tag{4.5}$$

and Ψ_i is the ground state of He. T is the transition operator which we always take in these calculations in the length form:

$$T = z_1 + z_2 \,.$$

The actual calculations use the $Q\Phi_n$ of our optimized 56-term calculation, the $\Psi_i(\vec{r}_1, \vec{r}_2)$ is the 20-term Hart-Hertzberg[21] function.

In Table III we give results for the width in which the rows correspond to the various approximations for $P\Upsilon_n(E_n)$. It can be seen that whereas the polarized orbital improves the result relative to experiment, the exchange adiabatic actually worsens the result. The reason for this can be seen from Fig. 1. With the radial functions corresponding to the various approximations, having the correct amplitude (normalization) at infinity, they are as pictured near the origin (which gives the major contribution to the matrix element) in Fig. 1. From Eq. (3.19) $\Psi^{(\text{pol})}$ is forced to be similar to $\Psi^{(\text{ex})}$ for most small values of r_1 [for which $r_1 < r_2$ primarily, so that $\epsilon(r_1 r_2) = 0$]. On the other hand, in the exchange-adiabatic approximation, the exchange polarization terms are omitted, and, as can be seen from Fig. 1, this has the effect of slackening this coercion thereby increasing $u_1(r)$ near the origin unnaturally. This finding is in accord with the nonresonant photoabsorption results of Bell and Kingston,[20] wherein it was also found that polarized orbital gave improved results.

TABLE III. Width of $^1P(1)$ auto-ionization state of He with various approximations for nonresonant continuum.

Nonresonant continuum approximation	V_1	V_2	Γ
Exchange	0.0288	0	0.0365
Exchange adiabatic	0.0296	-0.0014	0.0350
Polarized orbital	0.0306	-0.0014	0.0374
Experiment			0.038 ± 0.004 [a]

[a] Madden and Codling, Ref. 2.

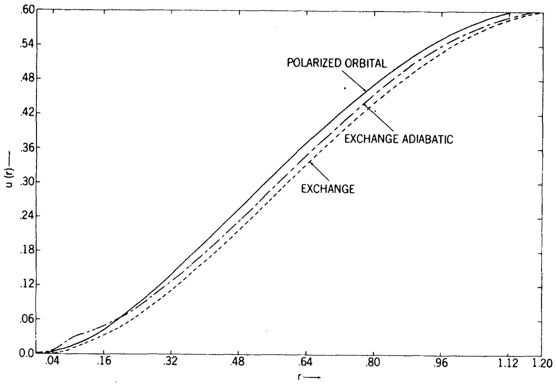

FIG. 1. Singlet P-wave e-He$^+$ scattering function in various approximations for $k = 1.617$. All functions are normalized to have amplitude k^{-1} at infinity. Lengths (r) are in Bohr radii.

Table IV contains the collected results using polarized orbital continuum functions for q as well as Γ. The δq are clearly non-negligible. The fact that they are positive is in accord with the qualitative argument of Fano.[13] The correction, however, is seen to lower our q value outside of the experimental range. Qualitatively it is easy to see that because the correction is of opposite sign to the main term that the value of q is a much more sensitive function of the nonresonant continuum function than either Δ or Γ. A 10% error in the main term can restore agreement with experiment. However, such a change in Δ will not alter our main conclusions with regard to the energy position as discussed in the next section.

Finally, we give in Table V a resume of our best calculated results together with other calculated results and experiments. The table also includes our values of the shift for those states for which we have calculated them. The continuum functions in the shift calculations were in the polarized orbital approximation. The last column contains new, as yet unpublished, results of Lipsky and Conneely. They are product hydrogenic functions which, since they contain no 1s states and very many configurations, supersede the results of Lipsky and Russek[22] and Altick and Moore.[23] Beyond the $n = 2$ states, their ^3P energies are seen to be slightly lower than our results, although for the lowest states they are substantially higher. Of particular note among the theoretical calculations is that of Burke and Taylor who used the traditional 3-term close-coupling

TABLE IV. Widths and q values for helium.

State	$\Gamma - \delta\Gamma$	$\delta\Gamma$	Γ	$q - \delta q$	δq	q
$^1P(1)$	0.037358	$+0.455 \times 10^{-4}$	0.037404	-2.657	0.382	-2.275
$^1P(2)$	1.165×10^{-4}	~ 0	1.17×10^{-4}	-8.413	1.567	-6.846
$^1P(3)$	0.010028	-0.408×10^{-4}	0.009987	-2.233	0.333	-1.900

expansion with 20 Hylleraas-type correlation terms in a direct scattering calculation. Although differences are slight between the two calculations, it will be of interest to see which results will turn out to be more correct, since they represent such different approaches to the resonance problem. The various results given in Table V are meant to be reasonably complete but by no means exhaustive.

V. MASS POLARIZATION

The last remaining strictly nonrelativistic correction is due to mass polarization. All other corrections (including spin-orbit coupling) are ultimately relativistic in origin. In the case of the bound states of He, the ground state in particular, the mass-polarization correction is comparable in magnitude to the spin-orbit terms. It is therefore completely justifiable to treat it in perturbation theory. Before doing a comparable thing for auto-ionization states some justification and reservations are in order.

The Q operator is derived from a P operator which relates to the asymptotic form of the scattering wave function. If for the moment we restrict ourselves to the scattering of electron from a neutral system (the two-electron case then corresponding to the composite system H^-), then the asymptotic form of the wave function in a coordinate system fixed in the center of mass is[24]

$$\lim_{\xi_1\to\infty} \psi = e^{i\vec{k}_i\cdot\vec{\xi}_1}\varphi_0(r_2) + f\frac{e^{ik_i\xi_1}}{\xi_1}\varphi_0(r_2). \qquad (5.1)$$

In the above f is the scattered amplitude, and the coordinates are defined as follows: with $\vec{\rho}_1$, $\vec{\rho}_2$, $\vec{\rho}_3$ being the coordinates of the two electrons and the nucleus in a space-fixed coordinate system, and $\vec{\rho}$ the center-of-mass coordinate of the target system:

$$\vec{\rho} \equiv (M\vec{\rho}_3 + m\vec{\rho}_2)/(M+m)\ , \qquad (5.2a)$$

we define the relative coordinates:

$$\vec{r}_1 = \vec{\rho}_1 - \vec{\rho}_3, \qquad (5.2b)$$

$$\vec{r}_2 = \vec{\rho}_2 - \vec{\rho}_3, \qquad (5.2c)$$

$$\text{and}\quad \vec{\xi}_1 = \vec{\rho}_1 - \vec{\rho} = \vec{r}_1 - \left(\frac{m}{M+m}\right)\vec{r}_2. \qquad (5.2d)$$

Clearly Eq. (5.1) is a solution of the asymptotic Hamiltonian ($\hbar = 1$):

$$H_{\text{asym}} = -\frac{1}{2\bar{\mu}}\nabla_{\xi_1}{}^2 - \frac{1}{2\mu}\nabla_{r_2}{}^2 + V(r_2), \qquad (5.3)$$

where μ is the reduced mass of the electron in the target system and $\bar{\mu}$ is the reduced mass of the second electron relative to the target:

$$\mu = mM/(M+m), \quad \bar{\mu} = m(M+m)/(M+2m). \qquad (5.4)$$

The total non–center-of-mass energy associated with this Hamiltonian is then

$$E = E_\mu + k_i{}^2/2\bar{\mu}\ , \qquad (5.5)$$

i.e., the reduced energy of the target plus the energy of the scattered electron relative to the target.

The advantage of the $\vec{\xi}_1$, $\vec{r}_2$ coordinates is, then, the fact that the asymptotic ψ is of the usual form Eq. (5.1), so that the correct P (hence Q) operator can readily be written down from

$$P_i = \varphi_0(\vec{r}_i) > < \varphi_0(\vec{r}_i{}')\delta(\vec{\xi}_j - \vec{\xi}_j{}'). \qquad (5.6)$$

The disadvantage, however, is that the residual potential is now quite complicated in these coordinates. That potential (now in rydbergs) is

$$-\frac{2Z}{r_1} + \frac{2}{r_{12}} = -\frac{2Z}{|\vec{\xi}_1 + \vec{r}_2\mu/M|} + \frac{2}{|\vec{\xi}_1 - \vec{r}_2(1-\mu/M)|}\ . \qquad (5.7)$$

In fact the direct evaluation of the increment of energy

$$\Delta\mathcal{E} = \int Q\Phi\left[Z\left(\frac{2}{\xi_1} - \frac{2}{|\vec{\xi}_1 + \vec{r}_2\mu/M|}\right)\right.$$
$$\left. -2\left(\frac{1}{|\vec{\xi}_1 - \vec{r}_2(1-\mu/M)|} - \frac{1}{|\vec{\xi}_1 - \vec{r}_2|}\right)\right]$$
$$\times Q\Phi(\vec{\xi}_1, \vec{r}_2)d^3\xi_1 d^3r_2 \qquad (5.8)$$

is a very difficult matter. In bound states therefore it is customary to write the kinetic energy in $\vec{r}_1$, $\vec{r}_2$ coordinates using

$$\frac{1}{2\bar{\mu}}\nabla_{\xi_1}{}^2 + \frac{1}{2\mu}\nabla_{r_2}{}^2 \to \frac{1}{2\mu}(\nabla_{r_1}{}^2 + \nabla_{r_2}{}^2)$$
$$-\frac{1}{M}\vec{\nabla}_{r_1}\cdot\vec{\nabla}_{r_2} \qquad (5.9)$$

and to compute the perturbation in the form

$$\Delta E = \frac{-2\mu}{M}\int \Psi(\vec{\nabla}_{r_1}\cdot\vec{\nabla}_{r_2})\Psi(\vec{r}_1, \vec{r}_2)\,d^3r_1 d^3r_2 \qquad (5.10)$$

which constitutes a very straightforward problem of integration. It can be shown in fact that Eq. (5.10) is equivalent to the counterpart of Eq. (5.8) for bound states; i.e., $Q\Phi \to \Psi$ where Ψ is a solution of

TABLE V. Compilation of theoretical and experimental results.

System and State	Resonance param- eters	This calculation	Madden and Codling (Ref. 2)	Burke and Taylor[a]	O'Malley and Geltman (Ref. 5)	Altick and Moore[b]	Burke and McVicar[c]	Other experi- mental results	Simpson, Mielizarek, and Cooper[d]	Lipsky and Conneely[e]
He $^1P(1)$	$\mathcal{E}$ (eV)	60.150			60.186	60.349				60.2733
	Δ (eV)	−0.007				−0.009				
	E (eV)	60.143	60.130 ± 0.015	60.149		60.340	60.269	60.0 ± 0.1[f]	60.1	
	Γ (eV)	0.0374	0.038 ± 0.004	0.0388		0.0365	0.044			
	q	−2.275	−2.80 ± 0.25			−2.97	−2.59			
$^1P(2)$	$\mathcal{E}$	62.757			62.777	62.784				62.7709
	Δ	$+0.719\times10^{-4}$				+0.007				
	E	62.757	62.756 ± 0.01			62.791	62.773			
	Γ	1.165×10^{-4}				1.59×10^{-4}	1.39×10^{-4}			
	q	−6.846				−3.70	−3.02			
$^1P(3)$	$\mathcal{E}$	63.679			63.712	63.709				63.6863
	Δ	−0.0021				−0.0017				
	E	63.677	63.653 ± 0.007			63.707	63.6905	63.5 ± 0.2[f]	63.6	
	Γ	0.010	0.008 ± 0.004			0.0070	0.0087			
	q	−1.900	−2.0 ± 1.0			−2.89	−2.44			
$^3P(1)$	$\mathcal{E}$	58.2838			58.300	58.41				58.3709
	Δ	0.0146								
	E	58.2984		58.317			58.360	58.34[g]	58.5	
	Γ	0.0084		0.0090			0.0106			
$^3P(2)$	$\mathcal{E}$	63.097			63.145	63.18				63.1303
	Δ									
	E						63.141			
	Γ	0.0027					0.0031			
$^3P(3)$	$\mathcal{E}$	63.274			63.931	63.29				63.2614
	Δ									
	E						63.276			
	Γ	5.3×10^{-5}					7.8×10^{-5}			
$^3P(4)$	$\mathcal{E}$	64.100			64.123	64.12				64.0777
	Δ									
	E						64.121			
	Γ	5.1×10^{-6}					4.6×10^{-6}			
$H^{-}\,^3P(1)$	$\mathcal{E}$	9.707			9.709					
	Δ	0.013								
	E	9.720		9.740				9.71 ± 0.03[h]		
	Γ	0.0063		0.0059				> 0.009		

[a] From P. G. Burke, in Invited Papers of the Fifth International Conference on the Physics of Electronics and Atomic Collisions, 1967 (University of Colorado Press, Boulder, Col., 1968), p. 128. Cf. also Proc. Phys. Soc. (London) 88, 549 (1966).

[b] Singlet results from Phys. Rev. 147, 59 (1966); triplet from Phys. Rev. Letters 15, 100 (1965).

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$$\left[-\frac{1}{2\mu}(\nabla_{r_1}{}^2+\nabla_{r_2}{}^2)-e^2\left(\frac{Z}{r_1}+\frac{Z}{r_2}-\frac{1}{r_{12}}\right)\right]\Psi=E_\mu\Psi. \tag{5.11}$$

The proof rests upon similar identities which are used in the proof of the virial theorem.[25] Unfortunately one cannot prove the equality of Eq. (5.8) to the projected counterpart of Eq. (5.10)

$$\Delta\mathcal{E}=\frac{-2\mu}{M}\int Q\Phi(\vec{\nabla}_{r_1}\cdot\vec{\nabla}_{r_2})Q\Phi d^3r_1d^3r_2. \tag{5.12}$$

This is because the projected equation which $Q\Phi$ satisfies is in reality quite different from Eq. (5.11).

In order to get an idea of how much Eq. (5.12) and Eq. (5.8) can be expected to differ from each other, it is appropriate to see to what extent the virial theorem is satisfied in the projected problem. The entries in Table VI give this comparison for the lowest ^1P auto-ionization state of He. Differences are seen to exist in the fourth significant figure, and they diminish as the number of terms in Φ increases. Thus one can have considerable confidence that the mass-polarization correction as we are evaluating it, via Eq. (5.12), must be very close to the correct expression Eq. (5.8). The direct evaluation of Eq. (5.12), which has proved to be an inordinately difficult task, is given in the last column of Table VI. It is smaller in magnitude than the ground (^1S) and first-excited (^1P) states which are 5.9×10^{-4} eV[10] and 1.7×10^{-4} eV[26]; we find therefore that the value of $\Delta\mathcal{E}$ from Eq. (5.12) does not give the requisite 10^{-2} eV necessary to reconcile our lowest ^1P energies with the central value of the experimental result.

Before concluding we would like to remark on two additional aspects of the mass-polarization problem. First we are neglecting the energy of the total center of mass. It can easily be seen that this amount of energy which is of the order of what the nucleus can absorb from a photon of momomentum $h\nu/c$ is of the order of 10^{-6} eV for the lowest ^1P resonance in He and is completely negligible for our purposes. The second point is that we have neglected any corrections in the mass polarization due to the $P\Psi$ part of the wave function. Although the mass-polarization term can be included exactly[24] in the framework of a scattering calculation (i.e., with the unprojected Hamiltonian), it would seem that for the Q-operator problem this contribution can be estimated by comparing the lifetime of the auto-ionization state with the transit time of an electron in approaching the target. Again for the ^1P state of He the two numbers are approximately 1.7×10^{-14} sec and 0.3×10^{-14} sec, respectively, with the latter being the time for an electron at the resonance energy to approach He$^+$ from a comfortable 100 Å distance. Thus this correction too would appear to be only a small part of $\Delta\mathcal{E}$.

Finally relativistic corrections should be even smaller than in the ground state by virtue of the fact that the kinetic energy in these doubly excited states is smaller.

In conclusion we find some satisfaction in the fact that this is the only calculation which is in agreement with the experimental result within the experimental error for the first two ^1P states of He. However, the discrepancy in the position of the lowest resonance from the mean experimental value is somewhat disconcerting, and we hope that this calculation will encourage an even further refinement of the experimental error.

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TABLE VI. Mass polarization and approximate validity of the virial theorem.

No. of terms	$2\mathcal{E}$ (Ry)	$\langle Q\Phi VQ\Phi\rangle$ (Ry)	Difference (Ry)	Mass polarization (10^{-4} eV)
10	−2.7619	−2.8820	−0.1201	1.04
20	−2.7713	−2.7677	0.0036	0.62
32	−2.7714	−2.7681	0.0033	0.60
56	−2.7716	−2.7687	0.0028	0.59

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Theory of Pressure Broadening of Microwave Spectral Lines

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A theory of pressure broadening of spectral lines is presented which is applicable to microwave spectra. It is an extension of the Anderson theory to the case of overlapping lines. The interference of neighboring lines is taken into account by the use of a relaxation matrix. The diagonal elements of this matrix correspond to linewidths and are calculated in the same way as in previous theories. The off-diagonal matrix elements are also calculated from the intermolecular interaction. Application is made to the ammonia and oxygen spectra.

INTRODUCTION

The phenomenon of pressure broadening of spectral lines has been extensively discussed in the literature.[1] The Van Vleck-Weisskopf[2] modification of the Lorentz theory has served as the standard line shape used in interpreting atomic and molecular absorption spectra. Foley[3] and Anderson[4] have shown how one may obtain the widths and shifts of spectral lines from a knowledge of the intermolecular potential. At low pressures, where individual spectral lines are isolated from each other, their theories have enjoyed much success. At high pressures, where the lines merge together to form a band, marked disagreement between experimental data and theory has been noted.

More recently, by extending Fano's[5] work on relaxation phenomena, Ben-Reuven[6] derived a general theory of microwave pressure broadening. He was able to account for overlapping lines by introducing a matrix which represented a quantum-mechanical interference term between the various transitions. A first principles calculation of these quantities has not been made, however.

In the present article a theory of pressure broadening of spectral lines is proposed which is meant to be applicable at all pressures. Three crucial approximations are employed: the binary collision assumption, the classical path approximation, and the impact approximation. The theory is compared with previous treatments and is shown to be a generalization of Anderson's[4] formalism. Finally the theoretical predictions