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Calculation of the $^1P(2s\,2p)$ Autoionization State of He with a Pseudostate Nonresonant Continuum*

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Previous Hylleraas calculations of $\mathcal{E} = \langle QHQ \rangle$ for the lowest ^1P autoionization state of helium are here supplemented by calculations of the shift (Δ), width (Γ), and shape parameter (q) using a $(1s, 2\tilde{p})$ pseudostate nonresonant continuum function. The function is constructed to eliminate the dominant $(2s, 2p)$ configuration of the autoionization state, while at the same time containing three variationally determined radial functions. Both Δ and q are also shown to contain contributions from the discrete part of the nonresonant spectrum, although quantitatively that contribution is found to be small. Final results change previous polarized-orbital results minimally, which means that the resonance position, $\mathcal{E} = \mathrm{E} + \Delta$, continues to be on the edge of the experimental error, and q remains somewhat outside the experimental result. Further relativistic corrections are briefly discussed, but a simple argument indicates that they are not likely to explain the differences with experiment. It is concluded that more-accurate experiments should be carried out.

I. INTRODUCTION AND FORMULAS

As has been previously emphasized,[1] the photo-"excitation" of the autoionization states of He afford a unique testing ground for precision checks of the continuum solutions of the Schrödinger equation. The basic parameters that are compared with experiment are the energy E, width Γ, and photoabsorption shape parameter q. The energy of the resonance is usually written[2] (rydberg units are used throughout)

$$E = \mathcal{E} + \Delta \,. \tag{1.1}$$

$\mathcal{E}$ is the result of a well-defined projection-operator variational calculation

$$\delta \frac{\langle \Phi Q H Q \Phi \rangle}{\langle \Phi Q \Phi \rangle} = 0 \,, \tag{1.2}$$

which we shall not discuss further except to repeat that a calculation of $\mathcal{E}$ to better than five-significant-figure accuracy has been carried out using a Hylleraas form for Φ with up to 84 linear terms.[1] The function Φ is then used for all further quadratures to calculate Δ, Γ, and q. Consider the expression[3] for Δ

$$\Delta = \langle \Phi H_{QP} G H_{PQ} \Phi \rangle , \tag{1.3}$$

where

$$H_{PQ} = PHQ , \tag{1.4}$$

etc., P and Q being the explicit projection operators for the one-electron target[4]:

$$P = P_1 + P_2 - P_1 P_2 , \tag{1.5a}$$

$$Q = 1 - P , \tag{1.5b}$$

$$P_i = \varphi_0(r_i) \rangle \langle \varphi_0(r_i) , \tag{1.5c}$$

and φ_0 is the He^+ ground-state wave function. The Green's function G in (1.3) is that associated with the nonresonant scattering equation at the resonant energy E,

$$(H' - E) G = \delta(\vec{r}_1 - \vec{r}_1{}') \delta(\vec{r}_2 - \vec{r}_2{}') . \tag{1.6}$$

If G is expanded in terms of the eigensolutions of the homogeneous equation

$$(H' - E') P\Upsilon = 0 , \tag{1.7a}$$

then G takes the form

$$G = \frac{1}{\pi} \sum_\nu \frac{P\Upsilon_\nu \rangle \langle P\Upsilon_\nu}{E_\nu{}' - E} + \frac{\mathcal{P}}{\pi} \int \frac{P\Upsilon(E') \rangle \langle P\Upsilon(E')}{E' - E} k' \, dE . \tag{1.8}$$

The principal-value ($\mathcal{P}$) integral in (1.8) indicates that we are using the standing-wave Green's function. The discrete sum then denotes the fact that (1.7a) may admit of a discrete spectrum

$$(H' - E_\nu{}') P\Upsilon_\nu = 0 , \tag{1.7b}$$

i.e.,

$$P\Upsilon_\nu = P\Upsilon(E_\nu{}') ,$$

in addition to its continuous solutions (1.7a). (H' will be discussed in Sec. II.) In the case of interest ($e + \mathrm{He}^+$) there are in fact an infinite number of such discrete states (as opposed to $e - \mathrm{H}$, wherein there is only one such state in the ${}^1S$ case).

Substitution of (1.8) into (1.3) then yields explicitly

$$\Delta = \frac{1}{2\pi} \left(\sum_\nu \frac{\Gamma_\nu}{E - E_\nu{}'} + \mathcal{P} \int \frac{\Gamma(E') dE'}{E - E'} \right) , \tag{1.3'}$$

where we shall abbreviate the two contributions

$$\Delta = \Delta_B + \Delta_C$$

and

$$\Gamma(E') = 2k' | \langle P\Upsilon(E') | H | Q\Phi \rangle |^2 . \tag{1.9a}$$

The normalization constant in (1.9a) assumes that the continuum solutions are normalized as plane waves at infinity (k^{-1} normalization). For the discrete part this reduces to

$$\Gamma(E_\nu{}') = 2 | \langle P\Upsilon_\nu | H | Q\Phi \rangle |^2 , \tag{1.9b}$$

with $P\Upsilon_\nu$ now quadratically normalized,

$$\langle P\Upsilon_\nu | P\Upsilon_\nu \rangle = 1 .$$

The function $\Gamma(E')$ is the width of the resonance when E' is equal to E:

$$\Gamma = \Gamma(E) . \tag{1.9c}$$

Although the continuum (principal value) part of Δ is well known,[5] the discrete contribution has not generally been exhibited nor calculated. Nevertheless, it is clearly necessary that this contribution be assessed in any calculation that presumes to deal accurately with Δ.

The discrete states also make a contribution to the (electromagnetic) shape parameter q. We exhibit here those formulas also:

$$q = q_0 + \delta q_B + \delta q_C , \tag{1.10}$$

$$q_0 = \mho^{-1} \langle Q\Phi | T | \Psi_0 \rangle , \tag{1.11a}$$

$$\delta q_B = (\pi \mho)^{-1} \sum_\nu \frac{\langle P\Upsilon_\nu | T | \Psi_0 \rangle V(E_\nu{}') k'}{E - E_\nu{}'} , \tag{1.11b}$$

$$\delta q_C = (\pi \mho)^{-1} \mathcal{P} \int_{-4}^{\infty} dE' \frac{\langle P\Upsilon(E') | T | \Psi_0 \rangle V(E') k'}{E - E'} , \tag{1.11c}$$

where $T = z_1 + z_2$ is the radiative transition operator and

$$\mho = k V(E) \langle P\Upsilon(E) | T | \Psi_0 \rangle , \tag{1.12}$$

$$V(E') = \langle P\Upsilon(E') | H | Q\Phi \rangle , \tag{1.13}$$

$$k' = (E' + 4)^{1/2}, \quad k = k' |_{E'=E} . \tag{1.14}$$

Ψ_0 is the wave function of the ground state of He. Again the explicit inclusion of the discrete contribution δq_B in addition to the continuum[5] will be considered for the first time.

II. PSEUDOSTATE NONRESONANT CONTINUUM

The nonresonant Hamiltonian H' in (1.6) and (1.7) is the full optical-potential Hamiltonian less the resonant term[3]:

$$H' = H_{PP} + \left(\sum_\mu{}' + \int d\mu \right) \frac{H_{PQ} | \Phi_\mu \rangle \langle \Phi_\mu | H_{QP}}{E - \mathcal{E}_\mu} , \tag{2.1}$$

where the prime on the summation indicates that the resonance being calculated (that Φ being unsubscripted) is omitted.

The first nontrivial approximation of the nonresonant equation quite obviously retains only H_{PP} in (1.7):

$$(H_{PP}-E')P\Upsilon_{\mathrm{ex}}=0\,. \tag{2.2a}$$

The equation is the well-known exchange-approximation equation[6]; its solutions have been calculated many times and in the ^1P case they may be written

$$\Upsilon_{\mathrm{ex}}=P\Upsilon_{\mathrm{ex}}=[u(r_1)/r_1]\frac{Y_{10}(\Omega_1)\varphi_{1s}(r_2)}{\sqrt{2}}+(1\longleftrightarrow 2). \tag{2.2b}$$

In (2.2b) we have also indicated the fact that Υ_{ex} is an eigenfunction of the P operator.

In considering corrections to (2.2) it is important to realize that the major contribution will be made by the continuum (which starts at the energy of the first excited state of the target) rather than the discrete terms in (2.1).[1] In fact, if the discrete resonances are much narrower than the separation between resonances, the discrete terms are negligible and only the continuum need be considered. That contribution is well known to be associated primarily with polarization,[7] so that a polarized-orbital wave function[8] naturally presents itself as a next approximation:

$$\Upsilon_{\mathrm{po}}=[u(r_1)/r_1]\frac{Y_{10}(\Omega_1)}{\sqrt{2}}[\varphi_{1s}(r_2)+\phi^{\mathrm{pol}}(r_1;r_2)]+(1\longleftrightarrow 2). \tag{2.3}$$

Both approximations (2.2) and (2.3) were calculated in Ref. 1; both gave very similar results which were only partially in agreement with experiment. We therefore consider here an even more elaborate nonresonant continuum function:

$$\sqrt{2}\,\Upsilon_{\mathrm{pss}}=\frac{F_1(r_1)}{r_1}Y_{10}(\Omega_1)\varphi_{1s}(r_2)+\sum_{l=0,2}\frac{F_l(r_1)}{r_1}\tilde{\varphi}_{2p}(r_2)\mathcal{Y}_{1l1}(\hat{r}_1,\hat{r}_2)+(1\longleftrightarrow 2), \tag{2.4}$$

where $\mathcal{Y}_{1l1}$ ($l=0,2$) are the two linearly independent vector couplings of odd parity that can form a total P state:

$$\mathcal{Y}_{1l1}(\hat{r}_1\hat{r}_2)=\sum_m(1lm-m\,|\,10)Y_{1m}(\Omega_1)Y_{lm}(\Omega_2)\,. \tag{2.5}$$

The function $\tilde{\varphi}_{2p}$ is the orthogonal part of the function $\bar{u}_{1s\to p}$ which accounts for the full polarizability of the He^+ target.

Letting

$$\bar{u}_{1s\to p}(r)=\left(\sqrt{\tfrac{1024}{129}}\right)e^{-2r}(r^3+r^2) \tag{2.6}$$

and

$$\tilde{u}_{1s\to p}(r)=[729(\sqrt{43})\bar{u}_{1s\to p}(r)-4096R_{2p}(r)]/\sqrt{6\,074\,747}\,, \tag{2.7}$$

where R_{2p} is (r times) the radial orbital of the $2p$ state,

$$R_{2p}(r)=2r^2e^{-r}/\sqrt{3}\,, \tag{2.8}$$

we have

$$\langle\tilde{u}_{1s\to p}(r),R_{2p}(r)\rangle=0\,. \tag{2.9}$$

The function $\tilde{\varphi}_{2p}$ in (2.4) is then

$$\tilde{\varphi}_{2p}=r^{-1}\tilde{u}_{1s\to p}(r)\,. \tag{2.10}$$

The motivation of (2.4) is as follows : Υ_{pss} is a modified pseudostate wave function[9] which is explicitly orthogonal to the $2s$ and $2p$ states of He^+. These are the states mainly responsible for the resonance; thus the function can be considered nonresonant in character and this is consistent with phase shifts in this approximation which are completely nonresonant in the energy range of the coefficient functions (F_1, F_0, F_2) and therefore it is much more capable of describing short-range correlations than Υ_{ex} or Υ_{po}. In fact, the latter also suffers from the fact that it contains contributions from the $2p$ state, even though it too gives rise to a nonresonant phase-shift behavior. Specifically,

$$\phi^{\mathrm{pol}}\propto-\frac{\epsilon(r_1r_2)}{r_1^2}\,\frac{\bar{u}_{1s\to p}(r_2)}{r_2}\,\frac{\cos\theta_{12}}{\sqrt{\pi}}\,.$$

Thus even in the limit $r_1\to\infty$, $\langle\phi^{\mathrm{pol}}\varphi_{2p}\rangle\neq 0$. [$\epsilon(r_1,r_2)$ is a step function.]

If we define a modified projection operator in the spirit of Miller,[10] $Q'=\chi'\rangle\langle\chi'$, where

$$r_1r_2\chi'=R_{2s}(1)R_{2p}(2)Y_{10}(\Omega_2)+R_{2s}(2)R_{2p}(1)Y_{10}(\Omega_1)\,,$$

it can be easily verified that $Q'\Upsilon_{\mathrm{pss}}=0$. This means that our nonresonant function is in P' ($=1-Q'$) space, which is a close approximation to the full P space of (1.5). In point of fact, operation with P yields

$$P\Upsilon_{\mathrm{pss}}=\{[F_1(r_1)/r_1]\,Y_{10}(\Omega_1)+I\,\tilde{\varphi}_{2p}(r_1)Y_{10}(\Omega_1)\}\varphi_{1s}(r_2)+(1\longleftrightarrow 2), \tag{2.11}$$

where

$$I=(4\pi)^{1/2}\int_0^\infty x\varphi_{1s}(x)F_0(x)\,dx\,. \tag{2.11b}$$

Thus all matrix elements that are evaluated depend explicitly on only two of the three coefficient functions in Υ_{pss}. (The third function, however, implicitly affects the other two by virtue

TABLE I. ^1P nonresonant phase shifts in the resonance region.

k^2 (Ry)	η (rad) Exchange	Polarized orbital	pss $(1s-\bar{2}\bar{p})$
2.40	−0.0574	−0.0233	−0.0312
2.45	−0.0564	−0.0224	−0.0298
2.50	−0.0555	−0.0215	−0.0284
2.55	−0.0545	−0.0206	−0.0270
2.60	−0.0538	−0.0197	−0.0257
2.65	−0.0527	−0.0187	−0.0243
2.70	−0.0520	−0.0178	−0.0229
2.75	−0.0503	−0.0169	−0.0215
2.80	−0.0496	−0.0160	−0.0200
2.85	−0.0488	−0.0151	−0.0185
2.90	−0.0480	−0.0141	−0.0169

of the dynamic coupling from the variational equations whose solution determined the F's.)

It is interesting to observe that had we started with an alternative form of the nonresonant function,

$$\Upsilon_{\text{ccpo}} = \frac{G_1(r_1)}{r_1} Y_{10}(\Omega_1)\varphi_{1s}(r_2) + \frac{G_0(r_1)}{r_1} Y_{10}(\Omega_1)\bar{\varphi}_{2p}(r_2)\cos\theta_{12}, \tag{2.12}$$

then operating with P would have yielded an expression identical to (2.11a), with the F's replaced by G's. Υ_{ccpo} is a special case of a closely coupled polarized-orbital wave function.[11] That approximation represents a somewhat different alternative to the merging of close coupling to polarized-orbital approximations from the pseudostate expansion.[9] In fact, Υ_{ccpo} is in accord with the prescription of Damburg and Karule.[12] Specifically, as Damburg[13] has recently brought out, Υ_{ccpo} (with $\bar{\varphi}_{2p}$ replaced by $r^{-1}\bar{u}_{1s\to p}$) is able to describe all of the long-range polarizability associated with $e-\text{He}^+$ scattering with only two undetermined functions. By contrast, the pseudostate (2.4) requires three undetermined functions, but by the same token it gives rigorously larger phase shifts. Thus its use in the present case cannot diminish the cogency of our results.

III. CALCULATION AND RESULTS

The integrodifferential equations resulting from Υ_{pss} were solved by an appropriate modification of the pseudostate program.[9] Numerical functions $F_l(r)$ are generated for $0<r\leqslant 15$. For larger values of r the functions $F_l(r)$ were generated from the asymptotic expansions

$$F_1(r) = \sin\theta\left(1+\frac{a_{11}}{r}+\frac{a_{21}}{r^2}+\cdots\right) + \cos\theta\left(\frac{b_{11}}{r}+\frac{b_{21}}{r^2}+\cdots\right) \tag{3.1a}$$

and (for $i = 0, 2$)

$$F_l(r) = \sin\theta\left(\frac{a_{2l}}{r^2}+\frac{a_{3l}}{r^3}+\cdots\right) + \cos\theta\left(\frac{b_{3l}}{r^3}+\cdots\right), \tag{3.1b}$$

where θ is the usual Coulomb argument

$$\theta = kr-(1/k)\ln 2kr - \tfrac{1}{2}\pi l + \sigma_l + \eta_l\,;$$

σ_l is the Coulomb phase factor $\arg\Gamma(1-i/k)$ and η_l is the residual phase shift.

The nonresonant phase shifts η_l in the resonance region are given in Table I, where they are compared with polarized-orbital and exchange-approximate phase shifts. We see that the $1s$-$2\bar{p}$ pseudostate phase shifts are nicely between the exchange-approximate phase shifts and the full polarized-

TABLE II. Γ, Δ, q in different approximations.

Nonresonant continuum	Exchange		Pseudostate		Polarized orbital
No. of terms in Q^{Φ}	56	84	56	84	56
Γ (eV)	0.0365	0.0363	0.0370	0.0369	0.0374
Δ_c (eV)	−0.007 37	−0.007 33	−0.007 44	−0.007 34	−0.007 00
Δ_B[a] (eV)	5.45×10^{-5}	5.46×10^{-5}			
q_0	−2.5235	−2.4513	−2.5181	−2.4734	−2.6566
δq_c	0.2413	0.2370	0.2385	0.2317	0.382
δq_B[a]	−0.0245	−0.0244			

[a] Bound-state contributions were only calculated in exchange approximations (see text). Exchange and polarized-orbital results from Ref. 1.

TABLE III. Comparison of ${}^1P(2s2p)$ results with experiment.

	Previous results		Present calculation	
Nonresonant continuum	Exchange	Polarized orbital	Pseudostate	Experiment[a]
Δ (eV)	−0.007 28	−0.006 95	−0.007 29	
E^b (eV)	60.1449	60.1452	60.1449	60.130 ± 0.015
Γ (eV)	0.0363	0.0374	0.0369	0.038 ± 0.004
q	−2.239	−2.274	−2.266	−2.80 ± 0.25

[a] Experimental results derived from Madden and Codling (Ref. 19) using $E = E$(max absorption) $- \Gamma/2q$.

[b] Results derived from $E = \mathcal{E} + \Delta$, with $\mathcal{E} = 60.152\,15$. This result is based on a newer value of the rydberg, $R_\infty = 13.605\,826$ eV, from B.N. Taylor, W.H. Parker, D.N. Langenberg, Rev. Mod. Phys. 41, 375 (1969). This value differs in the fifth significant figure from the older value used in Ref. 1, and accounts for the apparent differences with those results.

orbital values.[8] This is expected, since the (unincluded) $2p$ state alone accounts for 65% of the dipole polarizability.

The a_{ji} in Eq. (3.1) can be readily worked out from the asymptotic form of the differential equations satisfied by the F_i. For purposes of evaluating all the integrals involved, the range $0 < r < 40$ was found to be sufficient.

All integrals for the resonant quantities Γ, Δ, and q are seen to involve the resonant energy E, which is initially unknown. Since, however, Δ is small, it is an excellent approximation to let E equal $\mathcal{E}$ in these integrals; the error in Δ, for example, is of order Δ^2, which is negligible for our purposes. One can, nevertheless, do better by using this as the first stage of an iteration procedure which quickly converges. Such an iteration procedure was carried out for Δ in the exchange approximation for $P\Upsilon$, and Δ was found to change by one unit in the fourth place after the decimal point. The results in Tables II and III, however, always refer to the first iteration.

The major contribution to all principal-value integrals comes from the energy range surrounding the resonance energy. Furthermore, differences between the different nonresonant continuum functions are small; thus in all calculations we used the exchange approximation for regions of E' *outside* $2.4 \leq E' \leq 2.9$ (Ry). The various approximations, therefore, reflect differences in that energy region only. Specifically, this means that the bound-state components of $P\Upsilon$ were evaluated in the exchange approximation.[14] Here the squared matrix elements for large principal ν can easily be shown to go like ν^{-3} and it is precisely this behavior which makes the sums in (1.3′) and (1.11b) converge. It also enables the inclusion of the infinite sum, once the constant of proportionality has been determined. We found that it required $\nu \cong 5, 6$ for the ν^{-3} behavior to set in, and that whatever the discrete contributions were, they came only from the first couple of discrete terms. A resumé of results is given in Table II, both for 56- and 84-term resonant-state approximations[1] of $Q\Phi$. The points to notice are that the changes in going from one to another nonresonant continuum are very small and that the discrete contributions (Δ_B) to Δ are negligible and just barely significant (δ_{q_B}) to q. In the q calculations at 50-term Hylleraas function was used for the ground (${}^1S$) state of He. Final results are compared to experiment in Table III. As far as comparison with experiment is concerned, neither 56- not 84-term Hylleraas $Q\Phi$, nor any of the three nonresonant continua, including the very elaborate pseudostate wave function, make any difference within the experimental error. That means that although Γ agrees very well with experiment, E remains on the edge, and q remains outside of, the experimental error.

We believe that the present calculation represents the most accurate theoretical result thus far evaluated for the ${}^1P(2s2p)$ state. Burke and Taylor[15] have performed a full scattering calculation using a $(1s, 2s, 2p)$ close-coupling expansion plus Hylleraas correlation; however, they could include only 20 such terms. If one lowers their resonance energy (60.149 eV) by the same amount as $\mathcal{E}$ in going from 20 to 84 terms,[1] one estimates that the converged value of the resonance position would be approximately 60.145 eV, in good agreement with the present calculated result.

Dalgarno and co-workers[16,17] have performed a series of alternative bound-state-type calculations. One[16] of their original values, 60.133 eV, seemed to agree very well with the central value of the experiment; however, an alternative result,[16] plus later calculations,[17] gave results much closer to our own. Very recently, Dalgarno informed us that he expects his best result to agree essentially exactly with our value.

The only remaining nonrelativistic correction, the mass polarization, was examined in Ref. 1 and found to be utterly negligible for the accuracy in question. This leaves only relativistic corrections to be considered. Such corrections are no easy matter to calculate, even for true bound states. The most analogous state is the $^1P(1s2p)$ state of parahelium, for which the relativistic corrections were calculated[18] to be -0.0015 eV. A simple argument leads to the conclusion that the absolute magnitude of this correction should be smaller for the present $^1P(2s2p)$ state. Specifically, this state being spatially larger and having a total energy closer to zero, the kinetic energy of the electrons must be smaller than in the corresponding $^1P(1s2p)$ bound state. Since the relativistic corrections are proportional to $(v/c)^2$ of the electrons, they too should be smaller. (This argument assumes there are no accidental cancellations of different contributions in the relativistic corrections. We are not aware of any such cancellations.) The present conclusion, therefore, is that our energy value (in eV) should be correct to about two units in the fifth place. We believe, therefore, that a new and more accurate experimental measurement is warranted. A reduction by a factor of 10 in the experimental error would be desirable, but a factor of 5 would suffice. It will be interesting to see if such an experiment might also assign an altered value of q consistent with our calculation.

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