

Calculation of autoionization of He and H^- using the projection-operator formalism

A. K. Bhatia and A. Temkin

Theoretical Studies Group, Goddard Space Flight Center, National Aeronautics and Space Administration, Greenbelt, Maryland 20771

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Improved calculations of the first several autoionization states of the lower symmetries (1^3S , 1^3P^o , 1^3D^e) are reported. Unshifted energies are obtained by diagonalizing QHQ using a Hylleraas basis with more terms than used previously. Shifts, widths, and photoabsorption shape parameters q (where appropriate) are obtained with the additional use of exchange approximate nonresonant continuum functions. Our previous calculations of H^- resonances are recapitulated and slightly augmented by using various improved nonresonant continua and correcting small previous errors. Comparison with other calculations and experiments is made. The latter is very satisfactory except for the lowest $1P$ autoionization state of He for which a more accurate experimental result is required.

I. INTRODUCTION

In the course of several years and a number of publications we have carried forward a program of calculation of resonances of two-electron atomic systems using the projection-operator formalism.¹⁻⁴ This program was based on the existence of explicit projection operators for the two-electron system⁵; the major innovation of our calculation consisted of the introduction of Hylleraas coordinates to describe the resonant state.¹ To that was added the use in the first instance of the exchange approximation for the nonresonant continuum functions to calculate the width, shift, and, where appropriate, the q parameter associated with the electromagnetic excitation of the resonant state.² An important additional realization in this series of papers was the contribution of the discrete part of the nonresonant spectrum.^{3,4} That contribution was also calculated in the exchange approximation.

In addition to the exchange approximation, we explored several physically more inclusive and mathematically more sophisticated approximations of the continuum portion of the nonresonant spectrum: exchange adiabatic,² polarized orbital,² and polarized orbital pseudostate approximations.³ In general these more sophisticated continua did not materially change the exchange-approximate results. (An exception is the lowest $1S$ state of H^- ; see below.) In the course of the calculations, however, several small errors have been uncovered. Most of these errors have been corrected,^{3,4} and only in the case of H^- are they important. One remaining correction, recently pointed out by Bardsley and co-workers,⁶ requires the use of the rydberg for infinite mass (R_∞) rather than the reduced rydberg (R_M) for comparison of calculations with electron-impact resonance scattering experiments. The use of R_∞ comes about by virtue of an effective

cancellation of reduced-mass and center-of-mass effects. Thus we repeat our H^- results here with this additional correction and include results using some additional continua beyond the exchange-approximate one. (In the Appendix we derive this rydberg correction and additionally show that in photoabsorption, the reduced rydberg is the correct one.)

This allows us in Sec. IV, to assess the situation as it now exists. We shall come to the conclusion that the agreement between experiment and theory is, with one exception, satisfactory, but that the accuracy of both should be improved. From the theoretical side, calculations can only be improved by definitive lower-bound scattering calculations; nevertheless even at the present state, the comparison as regards the lowest $1P^o$ state of He is unsatisfactory and calls first for an experiment which reduces the error in the position by at least a factor of 5.

II. FORMULAS

In view of the fact that we have given all of the relevant equations in our previous papers, we shall only enumerate the final formulas here.

The unshifted energies are calculated from the variational principle

$$\delta \{ \langle \Phi_{LS} QH Q \Phi_{LS} \rangle / \langle \Phi_{LS} Q \Phi_{LS} \rangle \} = 0. \quad (2.1)$$

Φ_{LS} is an ansatz for the spatial part of a wave function [of angular momentum L , parity $(-1)^K$, spin S , where $S=0$ (singlet) or $S=1$ (triplet)]:

$$\begin{aligned} \Phi_{L,S}(\vec{r}_1, \vec{r}_2) = \sum_{\kappa} \{ & \cos(\frac{1}{2}\kappa\theta_{12}) [f_{L\kappa} + (-1)^S \tilde{f}_{L\kappa}] \mathfrak{D}_L^{\kappa+} \\ & + \sin(\frac{1}{2}\kappa\theta_{12}) [f_{L\kappa} - (-1)^S \tilde{f}_{L\kappa}] \mathfrak{D}_L^{\kappa-} \}; \end{aligned} \quad (2.2)$$

$\mathfrak{D}_L^{\kappa\pm}$ are exchange rotational harmonics of sym-

metric Euler angles⁷ and $f_{L\kappa}$ are "radial" functions which for Hylleraas calculations are of the form⁸

$$f_{L\kappa}(r_1 r_2 r_{12}) = e^{-(\gamma_\kappa r_1 + \delta_\kappa r_2)} r_1^{(L+\kappa)/2} r_2^{(L-\kappa)/2} \times \sum_{l,m,n}^N C_{lmn}^{(\kappa)} r_1^l r_2^m r_{12}^n \quad (2.3a)$$

and

$$\tilde{f}_{L\kappa}(r_1 r_2 r_{12}) = f_{L\kappa}(r_2 r_1 r_{12}). \quad (2.3b)$$

[The above assumes $(-1)^L = (-1)^\kappa$; if $(-1)^{L+1} = (-1)^\kappa$, then L is replaced by $L+1$ in (2.3a). The double prime on the sum in (2.2) indicates every second value of κ is to be included, i.e., only κ 's of the given parity.]

The number of eigensolutions which result from the variational calculation (2.1) is $N \times k$, where N is the number of linear parameters in (2.3a) and k is the number of different κ 's in (2.2). Each solution whose eigenenergy \mathcal{E}_λ is below the threshold for inelastic scattering corresponds to a resonance in the elastic scattering at energy \mathcal{E}_λ which is shifted by an ambient Δ_λ from \mathcal{E}_λ :

$$E_\lambda = \mathcal{E}_\lambda + \Delta_\lambda. \quad (2.4)$$

(λ represents the sequential order of the resonances; other quantum indices such as L and S are suppressed.) The resonance is also characterized by a width Γ , which theoretically is most easily expressed as the energy interval in which the phase shift η increases by π radians over its nonresonant value η_{nr} :

$$\eta = \eta_{nr} + \tan^{-1} \left[\frac{1}{2} \Gamma_\lambda / (E_\lambda - E) \right]. \quad (2.5)$$

Finally there is a shape parameter q which is associated with electromagnetic transitions (photoabsorption) from the ground state of the compound (electron and target) system to the resonant state. For an isolated resonance the photoabsorption profile can be represented by⁹

$$\sigma_\alpha = (q + \epsilon)^2 / (1 + \epsilon^2), \quad (2.6)$$

where

$$\epsilon = (E - E_\lambda) / \frac{1}{2} \Gamma_\lambda. \quad (2.7)$$

The photoabsorption shape parameter (q) is more specialized than the foregoing quantities in that it is usually (for experimental purposes) restricted to states which are dipole allowed from the ground state, whereas scattering resonances can occur in almost all angular momentum parity states.

The quantities Δ_λ , Γ_λ , and q_λ are, in addition to \mathcal{E}_λ , the fundamental quantities of the resonance calculations. As opposed to \mathcal{E}_λ , which relates solely to Φ_λ , the former three quantities depend also on a nonresonant continuum function $\Upsilon_\lambda(E')$.

For each resonant state λ the nonresonant functions span a continuum of energies E' and they may also include a discrete spectrum E'_ν as well. In the formulas which follow we shall suppress the λ index. (With regard to the nonresonant functions, all our approximations of Υ will in fact be independent of λ .) The continuous spectrum will be denoted by $\Upsilon(E')$ (normalized as plane wave at infinity), and the discrete spectrum by Υ_ν (assumed quadratically normalized to 1). All quantities may be expressed in terms of the following integrals:

$$\mathcal{T}(E') = \langle P \Upsilon(E') | T | \psi_0 \rangle, \quad (2.8a)$$

$$V(E') = \langle P \Upsilon(E') | H | Q \Phi \rangle, \quad (2.9a)$$

and their discrete counterparts

$$\mathcal{T}_\nu = \langle P \Upsilon_\nu | T | \psi_0 \rangle, \quad (2.8b)$$

$$V_\nu = \langle P \Upsilon_\nu | H | Q \Phi \rangle. \quad (2.9b)$$

In (2.8) ψ_0 is the ground state of the compound system and T is an electromagnetic transition operator. We shall only be concerned with helium as far as \mathcal{T} is concerned, so that ψ_0 is the ground (¹S) state of the helium atom; (taken as a 50-term Hylleraas expansion with one nonlinear parameter) T is taken as the dipole length operator:

$$T = z_1 + z_2.$$

In addition we define

$$\mathcal{T}_\phi = \langle Q \Phi | T | \psi_0 \rangle \quad (2.10)$$

and

$$\mathcal{U} = k V(E) \mathcal{T}(E). \quad (2.11)$$

The resonance parameters can then be given in terms of the above as follows (E is the resonance energy):

$$\Gamma \equiv \Gamma(E) = 2k |V(E)|^2, \quad (2.12)$$

$$\Delta = \frac{1}{2\pi} \left(\sum_\nu \frac{\Gamma_\nu}{E - E'_\nu} + \mathcal{P} \int_{I_1}^\infty \frac{\Gamma(E')}{E - E'} dE' \right), \quad (2.13a)$$

$$q = q_0 + \delta q_b + \delta q_c, \quad (2.14a)$$

where

$$\Gamma_\nu = 2\pi |V_\nu|^2, \quad (2.13b)$$

$$q_0 = \mathcal{T}_\phi / \mathcal{U}, \quad (2.14b)$$

$$\delta q_b = \mathcal{U}^{-1} \sum_\nu \frac{\mathcal{T}_\nu V_\nu}{E - E'_\nu}, \quad (2.14c)$$

$$\delta q_c = (\pi \mathcal{U})^{-1} \int_{I_1}^\infty dE' \frac{\mathcal{T}(E') V(E') k'}{E - E'}. \quad (2.14d)$$

The lower limit I_1 in (2.14d) is the start of the elastic scattering continuum, which is -4 Ry in

the case of $e + \text{He}^+$ (He) and -1 Ry in the case of $e + \text{H}$ (H^-). It should be realized that the discrete spectrum for H^- consists of only one state and only in the ^1S partial wave. Note also that the absence of a factor π^{-1} in (2.14c) represents an additional correction to Ref. 3 which was not contained in the erratum.³ [The factor k' in the numerator of (1.11) of Ref. 3 is a typographical error.]

Finally we record the explicit form of the projection operators:

$$P = P_1 + P_2 - P_1 P_2, \quad (2.15a)$$

$$Q = 1 - P, \quad (2.15b)$$

$$P_i = \phi_0(\nu_i) \langle \phi_0(\nu_i), \quad (2.15c)$$

where $\phi_0(\nu_i)$ is the ground-state wave function of the target system containing the i th electron ($i = 1$ or 2).

III. RESULTS

We give first our helium results. For S states the previous QHQ calculations have been improved by using two nonlinear parameters and $N = 84$ linear parameters for all states. (However, in the integral expressions for Γ and Δ we used an $N = 70$ one nonlinear parameter $Q\Phi$.) The nonresonant continuum functions here and in all other cases in

Table I are those of the exchange approximation except for the $^{1,3}D$ states as noted in footnote c of the Table. For the second and third eigenvalues of the 3P results we use the \mathcal{E} values of Chung and Chen.¹⁰ These are based on a configuration-interaction-type wave function and are slightly better than our present results as can be seen from footnote b. This indicates that the larger size of autoionization states rapidly dilutes the effectiveness of the short range r_{12} correlation. The D -state calculations¹¹ have only been altered by the inclusion of the bound-state contribution to the shift. It is evident that this contribution can exceed the continuum contribution in some cases.

As is indicated in footnote a of Table I the results have been converted to eV using R_∞ , because the rydberg for infinite mass is the appropriate one for comparison with $e\text{-He}^+$ collisional resonance experiments⁶ (Appendix). Such experimentally determined positions have been most completely compiled by Martin,¹² to which reference the reader is referred. In all cases the experimental results are in agreement with results of Table I within the experimental errors; the latter are quoted as being of the order ± 0.05 eV.

The $^1P^o$ results are not given in Table I because experimentally they are more accurately determined from photoabsorption experiments. Also

TABLE I. Summary of first four autoionization states of He of S , P , and D angular momentum (excluding 1P).

	λ	\mathcal{E}_λ (Ry)	\mathcal{E}_∞ (eV) ^a	Γ (eV)	Δ_c (eV)	Δ_b (eV)	Δ (eV)	E_∞ (eV)
1S	1	-1.557 626 5	57.8223	1.25×10^{-1}	1.177×10^{-2}	9.346×10^{-3}	2.112×10^{-2}	57.8435
	2	-1.245 497 1	62.0691	6.67×10^{-3}	5.307×10^{-3}	1.664×10^{-2}	2.195×10^{-2}	62.0911
	3	-1.180 159 7	62.9581	3.87×10^{-2}	3.355×10^{-3}	9.959×10^{-4}	4.351×10^{-3}	62.9624
	4	-1.096 467 8	64.0968	2.412×10^{-3}	1.478×10^{-3}	2.748×10^{-3}	4.226×10^{-3}	64.1010
3S	1	-1.205 210 7	62.6173	4.21×10^{-5}	4.73×10^{-8}	2.061×10^{-5}	2.066×10^{-5}	62.6173
	2	-1.119 533 2	63.7830	7.09×10^{-6}	1.97×10^{-5}	8.294×10^{-5}	1.026×10^{-4}	63.7831
	3	-1.097 699 0	64.0800	1.22×10^{-4}	6.60×10^{-5}	2.353×10^{-4}	3.013×10^{-4}	64.0803
	4	-1.065 025 9	64.5246	1.32×10^{-4}	3.24×10^{-6}	1.594×10^{-4}	1.626×10^{-4}	64.5247
3P	1	-1.522 983	58.2937	8.90×10^{-3}	1.455×10^{-2}	1.267×10^{-2}	2.720×10^{-2}	58.3209
	2	-1.169 776 ^b	63.0994	2.61×10^{-3}	5.013×10^{-3}	2.219×10^{-3}	7.232×10^{-2}	63.1066
	3	-1.158 012 ^b	63.2594	4.88×10^{-5}	4.730×10^{-6}	6.825×10^{-5}	7.298×10^{-5}	63.2595
1D	1	-1.405 634	59.8903	0.0729	0.0220 ^c	0.0023 ^c	0.0243	59.9146
	2	-1.138 752	63.5215	0.0187	0.0044	0.65×10^{-4}	0.0045	63.5259
	3	-1.112 855	63.8738	5.81×10^{-4}	1.815×10^{-4}	0.10×10^{-4}	1.915×10^{-4}	63.8740
	4	-1.073 241	64.4128	7.12×10^{-3}	1.667×10^{-3}	0.56×10^{-5}	1.673×10^{-3}	64.4145
3D	1	-1.167 611	63.1288	2.72×10^{-6c}	2.60×10^{-4c}	9.91×10^{-4}	1.25×10^{-3}	63.1301
	2	-1.121 361	63.7581	1.92×10^{-4}	9.17×10^{-5}	3.62×10^{-6}	9.53×10^{-5}	63.7582
	3	-1.083 336	64.2755	3.31×10^{-6}	1.20×10^{-4}	2.78×10^{-4}	3.98×10^{-4}	64.2759
	4	-1.066 831	64.5000	1.36×10^{-4}	5.02×10^{-5}	5.50×10^{-6}	5.57×10^{-5}	64.5001

^aResults in eV relative to the ground state of He $-5.807\,448\,75$ Ry [C. L. Pekeris Phys. Rev. **146**, 48 (1966)] using $R_\infty = 13.605\,826$ eV from B. N. Taylor, W. H. Parker, D. N. Langenberg, Rev. Mod. Phys. **41**, 375 (1969).

^bFrom Chen and Chung, Ref. 11. Our latest results for these eigenvalue are $-1.169\,462$ and $-1.157\,964$, respectively.

^c $^{1,3}D$ widths and Δ_c have been calculated with polarized orbital nonresonant functions (cf. Ref. 10). All other results utilize the exchange approximation (cf. text).

TABLE II. Summary of ¹P autoionization states of He.

Quantity \ State	¹ P(1)		¹ P(2)		¹ P(3)	
	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.
\mathcal{E} (Ry)	-1.385 789 5		-1.194 182 ^a		-1.127 716 ^a	
\mathcal{E}_M (eV) ^b	60.152 15		62.758 77		63.662 97	
Δ_c (eV)	-0.0073		0.719×10^{-4}		-0.0021	
Δ_b (eV)	1.715×10^{-4}		5.483×10^{-4}		0.853×10^{-4}	
Δ (eV)	-0.00713		6.202×10^{-4}		-0.0020	
E (eV)	60.1450	60.130 ± 0.015^d	62.7594	62.756 ± 0.01^c	63.660 96	63.653 ± 0.007^c
Γ (eV)	0.0363	0.038 ± 0.004	1.165×10^{-4}		0.010	0.008 ± 0.004
q_0	-2.4513					
δq_c	0.2370					
δq_b	-0.0767 ^d					
q	-2.2910	-2.80 ± 0.25				

^aValues taken from Chung and Chen, Ref. 13. Our values are -1.194 171 and -1.126 399, respectively (Ref. 21).

^bReduced rydberg $R_M = 13.603 976$ eV used in conversion.

^cExperimental values from Madden and Codling (Ref. 14).

^dValue has been corrected by factor π from Ref. 3 including erratum.

the theoretical result for this comparison requires use of the appropriate reduced rydberg, R_M (Appendix). It is because of the greater experimental accuracy that we have subjected these states to more extended calculation by utilizing several increasingly more sophisticated nonresonant contin-

uum approximations. The latest results are given in Table II. Our calculations of \mathcal{E} are those already reported² and again the upper two are replaced by those of Chung and Chen¹³ which are lower than ours (cf. footnote a). In this case because the experiment¹⁴ is more accurate, these

TABLE III. H⁻ resonances.

Our calculations \ State	¹ S			³ P		¹ D	
	Exch.	Ex.-ad.	Pol. orb.	Pol. orb.	Pol. orb.	Pol. orb.	Pol. orb.
\mathcal{E} (Ry)		-0.297 563			-0.285 196 9		-0.256 174
\mathcal{E}_∞ (eV) ^a		9.557 24			9.725 49		10.120 37
Nonresonant approx.							
Δ_c (eV)	-0.0066	-0.0046	-0.0027	0.0130	0.0040	0.0130	0.0040
Δ_b	+0.0033	0.0027	0.0019
$\Delta = \Delta_c + \Delta_b$	-0.0033	-0.0019	-0.0008	0.0130	0.0040	0.0130	0.0040
E (eV)	9.5539	9.5553	9.5564	9.7385	10.1244	9.7385	10.1244
Γ (eV)	0.0406	0.0436	0.0476	0.0063	0.010	0.0063	0.010
Other results		E	Γ	E	Γ	E	Γ
Scattering		9.5603	0.0475	9.7417	0.0059	10.1267	0.0088
Burke, Ref. 19							
Complex rotation I		9.5570	...				
Doolen <i>et al.</i> , Ref. 18							
Kohn variational		9.5574	0.0472				
Shimamura, Ref. 20							
Stabilization		9.5572	0.0559	9.7403	0.0049		
Bhatia, Ref. 18							
Q-projected Kohn		9.5542	0.0411				
Chung and Chen, Ref. 16							
Complex rotation II		9.5572	0.0474				
Bardsley and Junker, Ref. 21							
Nesbet and Lyons, Ref. 24		9.571	0.0492				
experiment							
Sanche and Burrow, Ref. 22		9.558	...	9.738	0.0056	10.128	0.0073
		± 0.010		± 0.010	± 0.0005	± 0.010	± 0.002

^aResult relative to ground state of H using $R_\infty = 13.605 826$ eV.

differences in \mathcal{E} are more significant in obtaining satisfactory agreement. For the lowest state we have examined three nonresonant continuum approximations. The results are very close to each other and have been given in Table II of Ref. 3. Thus we here confine ourselves to the exchange-approximate results while again emphasizing that the δq_b contribution has been corrected by a factor π as noted in footnote c. Nevertheless the final value q is somewhat outside the experimental error for the first state, and as can be seen the value of E is on the very edge of the experimental error.

We now turn to H^- . With regard to \mathcal{E} we use our best previous results which were obtained in Ref. 4 with one nonlinear parameter and $N = 70, 84$ for $^1S, ^3P$ states respectively. For D states the calculation also previously published¹¹ requires two independent "radial" functions: each was described with one nonlinear parameter and $N = 56$ linear parameters.¹¹ The results are given in Table III, where they are compared with the best previous calculations. For comparison with experiment the reader is referred to a recent article of Risley, Edward, and Geballe¹⁵ which contains a fairly complete compilation of results plus theoretical calculations. Unfortunately the calculations have been converted to eV using R_M instead of R_∞ . Suffice it to say that use of R_∞ which amounts to a $+0.008$ -eV shift upward in the theoretical results removes the previous appearance of calculated results to be low compared to experiment. Within the lesser accuracy of the experiment the agreement can now be described as definitely satisfactory. Discrepancies that now exist are on a smaller scale and are significant only among the calculations themselves (cf. Table III).

From the point of view the present type of projector operator calculation the 1S resonance of H^- presents a special problem. For in calculating the shift, there is one bound-state contribution, and this tends to cancel the continuum contribution—how much depends sensitively on the approximation of the nonresonant functions used. Three calculations are shown in Table III. Whereas the exchange approximation tended to support the Q -projected Kohn calculation of Chung and Chen¹⁶ as we previously reported,⁴ the use of polarization approximations, which results we now include, gives more cancellation between Δ_b and Δ_c and raises the value of E more in the direction of the newer complex rotation and stabilization calculations.^{17,18} We believe that the best present calculations show the position of the 1S resonance to be 9.556 ± 0.002 eV and that as yet no calculation can claim to be more definitive than indicated by that error. This 1S calculation plus 3P and 1D results is given in Table

III together with a selection of other calculated results using other methods.¹⁹⁻²¹ In addition we include the experimental results of Sanche and Burrow²² which still appear to us to stand out as the most precise experimental determinations of the resonance structure. Even so one can see that the errors are such that they really do not allow a definitive selection of the best theoretical calculations.

IV. CONCLUSION

In general the agreement between calculations based on the projection operator formalism and experiment is satisfactory. The most glaring exception is the lowest 1P autoionization state of He (Table II). The insensitivity of Δ to the approximation for the nonresonant continuum³ makes it unlikely that an error can be attributed to it. The convergence of the QHQ calculation⁴ as supported by other configuration-interaction-type calculations¹³ renders the value of \mathcal{E} even more secure in this case. On the other hand the experimental error, considering that it refers to a photoabsorption experiment,¹⁴ is surprisingly large. We therefore feel that the first priority is for a reduction of that error.

From the theoretical point of view, one now requires in effect a definitive scattering calculation. When such a calculation is carried out in the resonance region, omission of the resonance term in the expansion of the optical potential gives a definitive calculation of the nonresonant continuum, and with such a nonresonant function the projection operator formalism can be carried out; but it then becomes a convenient alternative way of doing the scattering calculation itself. Such calculations are under way in this laboratory both for the resonant and nonresonant scattering; a preliminary report of the latter has been given.²³ This paper therefore concludes our present program of projection operator resonance calculations for two-electron systems.

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APPENDIX

We consider here the energy that is appropriate for the comparison of theory with experiment in the two main types of resonant measurements (a) photoabsorption and (b) electron scattering. Both reactions can be written

$$a + T = C, \quad (\text{A1})$$

where a is the impinging particle (photon or electron), T is the target, and C is the resonant state of the compound system. In both cases we envisage the target (atom or ion) to be initially at rest in the laboratory frame:

$$E_T^{\text{total}} = E_T^{\text{int}} = E_T^{\text{lab}}, \quad (\text{A2})$$

where E^{int} is the internal energy (i.e., that computed with R_M). Thus the total momentum is just that of the incident particle a . Conservation of momentum and energy (in the laboratory frame) then gives

$$E_a + E_T^{\text{int}} = E_c^{\text{total}}, \quad (\text{A3})$$

$$p_a = P_c,$$

$$E_c^{\text{total}} = E_c^{\text{int}} + P_c^2/2M_c, \quad (\text{A4})$$

where P_c is the (magnitude of the) momentum and M_c the mass of the compound system in the lab frame. We now consider the two cases separately:

(i) $a = \text{photon}$, then

$$E_a = h\nu, \quad p_a = h\nu/c. \quad (\text{A5})$$

Here (A3) and (A4) reduce to

$$h\nu + E_T^{\text{int}} = E_c^{\text{int}} + P_c^2/2M_c, \quad (\text{A6})$$

$$h\nu/c = P_c, \quad (\text{A7})$$

from which solving for $h\nu$ we find trivially

$$h\nu = \frac{E_c^{\text{int}} - E_T^{\text{int}}}{1 - h\nu/2M_c c^2}. \quad (\text{A8})$$

Since $h\nu \ll 100$ eV and $2M_c c^2 > 10^9$ eV for essentially all cases of interest (in particular H⁻ and He), (A8) is equivalent (to better than seven significant figures) to

$$h\nu = E_c^{\text{int}} - E_T^{\text{int}}. \quad (\text{A8}')$$

(A8) says that for photoabsorption measurements the experimental measurements are to be compared with theory using R_{M_c} and to great accuracy M_c can be replaced by M_T .

(ii) $a = \text{electron}$, then

$$E_a = \frac{1}{2}m_e v^2, \quad p_a = m_e v. \quad (\text{A9})$$

In this case (A3) and (A4) reduce to ($m = m_e$)

$$\frac{1}{2}m v^2 + E_T^{\text{int}} = E_c^{\text{int}} + P_c^2/2M_c, \quad (\text{A10})$$

$$m v = P_c, \quad (\text{A11})$$

which can be solved as

$$\frac{1}{2}m v^2 = \frac{E_c^{\text{int}} - E_T^{\text{int}}}{1 - m/M_c}. \quad (\text{A12})$$

But now, we observe that

$$E_{c,T}^{\text{int}} = \frac{E_{c,T}^{(\infty)}}{1 + m/M_{c,T}}, \quad (\text{A13})$$

where $E^{(\infty)}$ refers to energy computed using R_∞ .

And using again the fact that

$$M_c = M_T + O(m), \quad (\text{A14})$$

we see that

$$\frac{1}{2}m v^2 = \frac{E_e^{(\infty)} - E_T^{(\infty)}}{1 - (m/M_T)^2} + O(m/M_T)^2, \quad (\text{A15})$$

or finally

$$\frac{1}{2}m v^2 = E_e^{(\infty)} - E_T^{(\infty)} + O(m/M_T)^2. \quad (\text{A16})$$

This says that (again to about seven significant figures) the electron impact resonant energy is the difference of autoionization and target-state energies computed with infinite rydberg (R_∞).

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