

Theory of Electron Capture in H⁺-H Collisions*

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The theory of electron capture in H⁺-H collisions at kilovolt energies is developed. A strong coupling is assumed between the electron ground states in the target and scattered atoms. The method depends on an approximation which amounts to neglecting terms of order K^{-1} compared to 1, where K is the wave number in atomic units for the collision of the two protons. Calculations are made for lab energies from 0.6 to 50 keV and the results compare favorably with the experimental results of Lockwood and Everhart. The center-of-mass correction accounts for the damping of resonances and otherwise produces a considerable effect. The method is applied to developing a formula for the relative probability for capture into an excited state. It is estimated that this probability is small.

1. INTRODUCTION

WHEN an ion with energy in the kilovolt range is incident on atoms or molecules, the probability that it will capture an electron from a target atom or molecule has been measured in a number of cases.¹⁻³ The plot of a typical differential cross section for electron capture versus energy of the incident ion exhibits pronounced resonances. This suggests a strong coupling between certain states for the electron in the target atom and those for the electron in the incident ion. In Sec. 2 the cross section for electron capture in the collision of a proton with a hydrogen atom is calculated on the assumption that in such a collision the ground states of the electron in the target and incident nuclei are strongly coupled together, and that other states may be disregarded. The method used depends upon the fact that at these high energies the wavelength for the motion of the colliding nuclei is small compared to the size of the atom. The results of a calculation are compared with experiment. In Sec. 3 the application of the strong coupling method is justified. The dependence on scattering angle and the effect of the center-of-mass correction are discussed. [Note added in proof. The center-of-mass correction referred to in this paper is equivalent to taking into account the momentum of the electron.] Reference is made to Appendix II where the method is applied to finding the probability for capture into an excited state.

This problem has been considered in recent years by a number of investigators.⁴⁻¹² The methods they

use are essentially perturbation methods or various modifications of the Born approximation. Some base their calculations on electron eigenfunctions of a quasi-molecule while others use atomic eigenfunctions. The method used here is a perturbation method in a different sense since the emphasis is placed on the nuclei. The Coulomb wave function which represents the collision of two protons gets modified by the presence of the electron. The usual boundary condition that the wave function represent an incident and a scattered wave is sufficient to determine the relative magnitude of the components of the capture and the noncapture states that make up the scattered wave.

2. THEORY AND CALCULATIONS

The Schrödinger equation for the collision of a proton with a hydrogen atom is

$$\left(-\frac{\hbar^2}{M}\nabla_{R'}^2 + \frac{\hbar^2}{2m}\nabla_{r_1}^2 - \frac{e^2}{R} + \frac{e^2}{r_1} + \frac{e^2}{r_2} + E \right) \Psi = 0, \quad (1)$$

where M is the nucleon mass, r_1 , r_2 , are the distances of the electron from nuclei 1 and 2, the target and incident nuclei, respectively, R' is the distance from the c.m. of the target hydrogen atom to 2, and R is the distance from 1 to 2. A general approach in solving this equation is to expand Ψ in terms of the eigenstates ψ_i of the hydrogen atom,¹³ i.e.,

$$\Psi = \sum_i F_i(R') \psi_i(r_1).$$

On substituting this into the Schrödinger equation and using the orthogonality property of the ψ_i 's, we are led to a differential equation for $F_i(R')$ which is the Schrödinger equation for a Coulomb field e^2/R together with an interaction term, $V_{\text{int}}^i(R') = \sum_m F_m(R') \int r_2^{-1} e^2 \psi_i^* \psi_m dr_1$. For the region $R' \ll$ the Bohr radius a_0 , the sum \sum_m of V_{int}^i contains a significant contribution only from the

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¹ F. P. Ziemba, G. J. Lockwood, G. H. Morgan, and E. Everhart, Phys. Rev. **118**, 1552 (1960).

² G. J. Lockwood and E. Everhart, Phys. Rev. **125**, 567 (1962).

³ P. R. Jones, P. Costigan, and G. Van Dyk, Phys. Rev. **129**, 211 (1963).

⁴ A. Dalgarno and H. N. Yadav, Proc. Phys. Soc. (London) **A66**, 173 (1953).

⁵ H. Schiff, Can. J. Phys. **32**, 393 (1954).

⁶ E. F. Gurnee and J. L. Magee, J. Chem. Phys. **26**, 1237 (1957).

⁷ D. R. Bates and R. McCarroll, Proc. Roy. Soc. (London) **A245**, 175 (1958).

⁸ D. R. Bates and N. Lynn, Proc. Roy. Soc. (London) **A253**, 141 (1959).

⁹ R. H. Bassel and E. Gerjuoy, Phys. Rev. **117**, 749 (1960).

¹⁰ A. F. Ferguson, Proc. Roy. Soc. (London) **A246**, 540 (1961).

¹¹ R. McCarroll, Proc. Roy. Soc. (London) **A246**, 547 (1961).

¹² D. R. Bates, *Atomic and Molecular Processes* (Academic Press Inc., New York, 1962), p. 549.

¹³ N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, London, England, 1949), 2nd ed., Ch. VIII.

term $m=l$ because of the orthogonality of the ψ 's. This circumstance uncouples the equations in the F_i 's and leaves them all as Schrödinger equations with a Coulomb field. For the range of collision energies spanned by our calculations, 0.6 to 50 keV (lab system), Ka_0 varies from 140 to 1300, where K is the wave number for the colliding particles in the c.m. system. We can therefore find an R' which simultaneously satisfies the two conditions, $R' \ll a_0$ and $KR' \gg 1$, for the range of K corresponding to the range of energies that will concern us. This means that the solution starts out from $R'=0$ as a Coulomb scattered wave and reaches the asymptotic value of a Coulomb wave within the region $R' \ll a_0$. Of course, when R' extends beyond this region, Ψ gets modified due to V_{int} .

We shall assume for Ψ not the general superposition of states discussed above; rather, we write

$$\Psi = F_0(R')\psi_0(r_1) + F_c(R'')\psi_0(r_2), \quad (2)$$

F_0 and F_c being the amplitudes for the electron in the initial and capture ground state, respectively; \mathbf{R}'' , appropriately, is the distance from nucleus 1 to the center of mass of nucleus 2 and the electron. [The term $F_c(R'')\psi_0(r_2)$ is contained in the general expansion of the type $\sum_i F_i(R')\psi_0(r_1)$.] Since Ψ starts out from the origin as a Coulomb wave and is modified over the atomic dimension by a slowly varying interaction energy V_{int} , it is natural to assume for F_0 and F_c , as we do below, a Coulomb wave modified slowly over the extent of the atom; but the rapidly varying part of the Coulomb wave, namely, $\exp(i\mathbf{K}\cdot\mathbf{R})$ or $\exp(iKR)$, is retained. Now

$$\mathbf{R}' = \mathbf{R} - \mathbf{r}_1 m M^{-1}$$

and

$$\mathbf{R}'' = \mathbf{R} - \mathbf{R} m M^{-1} + \mathbf{r}_1 m M^{-1},$$

and, therefore,

$$\begin{aligned} \mathbf{K}\cdot\mathbf{R}' &\approx \mathbf{K}\cdot\mathbf{R} - k\mathbf{r}_1\cdot\hat{\mathbf{R}}, \\ KR' &= KR - k\mathbf{r}_1\cdot\hat{\mathbf{R}}, \\ KR'' &= KR + k\mathbf{r}_2\cdot\hat{\mathbf{R}}, \\ k &= KmM^{-1}, \end{aligned} \quad (3)$$

where the first equation holds very approximately for the case we calculate in this section, namely, small angle scattering. In view of Eq. (3) and the above remarks about the mathematical form of Ψ , we may write

$$\begin{aligned} F_0(R') &= F_0(R) \exp(-ik\mathbf{r}_1\cdot\hat{\mathbf{R}}) \\ F_c(R'') &= F_c(R) \exp(ik\mathbf{r}_2\cdot\hat{\mathbf{R}}). \end{aligned} \quad (4)$$

We substitute in Eq. (1) the Ψ of Eqs. (2) and (4), multiply the resulting equation by $\psi_0(r_1) \exp(ik\mathbf{r}_1\cdot\hat{\mathbf{R}})$ and integrate over \mathbf{r}_1 . This gives the equation

$$\begin{aligned} (\nabla^2 + K^2 - 2\alpha KR^{-1})F_0(R) \\ + 2\alpha K[V_{00}(R)F_0 + V_{0c}(R)F_c] = 0, \end{aligned} \quad (5)$$

where $\alpha = e^2/\hbar v$, v being the relative velocity of the two nuclei, and

$$V_{00}(R) = \int r_2^{-1} \psi_0^2(r_1) d\mathbf{r}_1, \quad (6a)$$

$$V_{0c}(R) = \int r_1^{-1} \psi_0(r_1) \psi_0(r_2) \exp[ik(\mathbf{r}_1 + \mathbf{r}_2)\cdot\hat{\mathbf{R}}] d\mathbf{r}_1. \quad (6b)$$

We may, in the same manner, expand Ψ around nucleus 2; i.e., we substitute for Ψ in Eq. (1) as above, multiply the resulting equation by $\psi_0(r_2) \exp(-ik\mathbf{r}_2\cdot\hat{\mathbf{R}})$, and integrate over \mathbf{r}_2 . We then obtain the equation

$$\begin{aligned} (\nabla^2 + K^2 - 2\alpha KR^{-1})F_c(R) \\ + 2\alpha K[V_{00}(R)F_c + V_{0c}^*(R)F_0] = 0. \end{aligned} \quad (7)$$

The coupled Eqs. (5) and (7) can be readily solved by a method described by Mott and Massey for the case of the strong coupling of two states in exact resonance.¹⁴ By adding and subtracting these two equations we get the following equations:

$$\begin{aligned} (\nabla^2 + K^2 - 2\alpha KR^{-1})(F_0 + F_c) \\ + 2\alpha K(V_{00} + V_{0cR})(F_0 + F_c) \\ + i2\alpha K V_{0cI}(F_0 - F_c) = 0, \end{aligned} \quad (8a)$$

$$\begin{aligned} (\nabla^2 + K^2 - 2\alpha KR^{-1})(F_0 - F_c) \\ + 2\alpha K(V_{00} - V_{0cR})(F_0 - F_c) \\ - i2\alpha K V_{0cI}(F_0 + F_c) = 0, \end{aligned} \quad (8b)$$

$$V_{0cR} \equiv \text{Re}(V_{0c}); \quad V_{0cI} \equiv \text{Im}(V_{0c}^*). \quad (9)$$

We assume solutions of the form

$$F_0 + F_c = \frac{1}{2}I + \frac{1}{2}Sf(\vartheta) \exp[i\varphi_+(R) + g_+(R)], \quad (10)$$

$$F_0 - F_c = \frac{1}{2}I + \frac{1}{2}Sf(\vartheta) \exp[i\varphi_-(R) + g_-(R)], \quad (11)$$

where $I + Sf(\vartheta)$ is the Coulomb solution in the asymptotic region.¹⁵ The function I is essentially the incident wave part, $\exp(i\mathbf{K}\cdot\mathbf{R})$, and S is essentially the scattered wave part, $\exp(iKR)/R$, of the Coulomb field solution. The function of the scattering angle, $f(\vartheta)$, is the Rutherford scattering amplitude.

The solution given by Eqs. (10) and (11) satisfies the required boundary conditions, namely, that at infinity F_0 become the sum of a plane wave and a scattered wave and F_c become purely a scattered wave. Furthermore, in view of the arguments preceding and following Eq. (2), the solutions to Eqs. (8a) and (8b) for $R \ll a_0$ are the Coulomb field solutions $I + Sf(\vartheta)$, so that as $R \rightarrow 0$, φ_{\pm} and g_{\pm} go to zero. On substituting the solution given by Eqs. (10) and (11) into Eqs. (8a) and (8b) and neglecting terms of order K^{-1} , we find that φ_{\pm} and g_{\pm} must satisfy the following differential

¹⁴ Reference 13, p. 146.

¹⁵ W. Gordon, Z. Physik 48, 180 (1928); also Ref. 13, p. 46.

equations:

$$[-\varphi_+' + ig_+' + \alpha(V_{00} + V_{0cR})] \exp(i\varphi_+ + g_+) + i\alpha V_{0cI} \exp(i\varphi_- + g_-) + \Phi_+ = 0 \quad (12)$$

$$[-\varphi_-' + ig_-' + \alpha(V_{00} - V_{0cR})] \exp(i\varphi_- + g_-) - i\alpha V_{0cI} \exp(i\varphi_+ + g_+) + \Phi_- = 0 \quad (13)$$

$$\Phi_{\pm} = 2I[Sf(\vartheta)]^{-1}[\alpha(V_{00} \pm V_{0cR}) \pm i\alpha V_{0cI}].$$

The prime indicates the operator d/dR .

As a first approximation to the solution of the coupled differential equations (12) and (13) we take

$$-\varphi_{\pm}' + \alpha(V_{00} \pm V_{0cR}) = 0, \quad (14)$$

$$g_{\pm}' \exp(g_{\pm}) \pm \alpha V_{0cI} \exp(g_{\mp}) = 0. \quad (15)$$

Equation (14) follows approximately from Eqs. (12) and (13) because V_{0cI} is small compared to V_{00} or V_{0cR} and because g_{\pm}' is small compared to the quantities of Eq. (14). Also, the terms Φ_{\pm} have many oscillations over a Bohr radius and they therefore contribute negligibly when Eq. (14) is integrated. This integration gives

$$\varphi_{\pm} = \varphi_0 \pm \varphi,$$

$$\varphi_0(R) = \alpha \int_0^R V_{00} dR, \quad (16)$$

$$\varphi(R) = \alpha \int_0^R V_{0cR} dR.$$

Equation (15) with the upper sign is obtained by multiplying Eq. (12) by $\exp(-i\varphi_0)$, subtracting from it Eq. (14), and taking the imaginary part of the resulting equation. The term in Φ_+ is discarded for the same reason as above. Equation (15) with the lower sign is obtained in the same manner from Eq. (13).

To solve Eq. (15) we first multiply the equation with the upper sign by $\exp(g_+)$ and the one with the lower sign by $\exp(g_-)$ and add the two resulting equations, giving,

$$\exp(g_+) \frac{d}{dR} [\exp(g_+) + \exp(g_-)] - \frac{d}{dR} [\exp(g_-)] = -\frac{1}{2} \frac{d}{dR} [\exp(2g_+) + \exp(2g_-)] = 0. \quad (17)$$

$$\therefore \exp(2g_+) + \exp(2g_-) = \text{const} = 2,$$

since 2 is the value of the constant near $R=0$. Equation (15) now becomes

$$[2 - \exp(2g_{\pm})]^{-1/2} \frac{d}{dR} [\exp(g_{\pm})] = \frac{d}{dR} \{\sin^{-1}[\exp(g_{\pm})/\sqrt{2}]\} = \mp \alpha V_{0cI}$$

and therefore,

$$\exp[g_{\pm}(R)] = \sqrt{2} \sin \left[\frac{1}{2} \pi \mp \alpha \int_0^R V_{0cI} dR \right]. \quad (18)$$

We are now in a position to calculate the relative probability for electron capture P_0 . From Eqs. (10), (11), and (16) we find the absolute probability for electron capture, $|F_c|^2$, given by the equation

$$|F_c|^2 = \frac{1}{4} |f(\vartheta)|^2 |\exp(i\varphi_0)|^2 \times [\exp(i\varphi_+ + g_+) - \exp(-i\varphi_+ + g_-)]^2.$$

By definition the relative probability is given by

$$P_0 = |F_c|^2 / (|F_c|^2 + |F_0|^2).$$

Since by our assumption we have $|F_0|^2 + |F_c|^2 = |f(\vartheta)|^2$,

$$P_0 = \frac{1}{4} \{ \cos^2 \varphi [\exp(g_+) - \exp(g_-)]^2 + \sin^2 \varphi [\exp(g_+) + \exp(g_-)]^2 \}. \quad (19)$$

The φ and g_{\pm} which appear in this equation and which are given by Eqs. (16), (18), (6b), and (9) are to be evaluated at $R=\infty$. These quantities are evaluated in Appendix I. According to Eqs. (16) and (A3)

$$\varphi = 2\alpha(1+k^2)^{-2}. \quad (20)$$

The energies corresponding to the maxima and minima of P_0 are, according to Eq. (19), given by solving for k in the equation

$$2\alpha/(1+k^2)^2 = \frac{1}{2} n\pi, \quad (21)$$

with odd n 's corresponding to maxima and even n 's to minima. We use atomic units for all quantities and in those units

$$k = 0.100 (E_{\text{lab}} \text{ in keV})^{1/2}.$$

A useful relation in these units is $\alpha k = \frac{1}{2}$, and this enables us to write Eq. (21) as

$$1/[k(1+k^2)^2] = \frac{1}{2} n\pi, \quad (22)$$

n being an integer.

The energies given by Eq. (22) are displayed in the upper and lower parts of the graph in Fig. 1, together with reference marks. The theoretical curve of Fig. 1 was calculated on the basis of Eq. (19). The quantities φ and g_{\pm} were taken in the first approximation, as represented by Eqs. (16), (18), (A3), and (A5).

Second approximation to φ and g_{\pm} . From Eqs. (12), (13), and (16) we may write:

$$\begin{aligned} & -[\varphi_+' + \alpha(V_{00} + V_{0cR})] + ig_+' + i\alpha V_{0cI} \\ & \quad \times \exp(-i2\varphi_+ + g_- - g_+) + \Phi_+ \exp(-i\varphi_+ - g_+) = 0, \\ & -[\varphi_-' + \alpha(V_{00} - V_{0cR})] + ig_-' - i\alpha V_{0cI} \\ & \quad \times \exp(i2\varphi_+ + g_+ - g_-) + \Phi_- \exp(-i\varphi_- - g_-) = 0. \end{aligned}$$

To proceed to a second approximation we let

$$\varphi_{\pm}' = \varphi_{1\pm}' + \Delta\varphi_{\pm}',$$

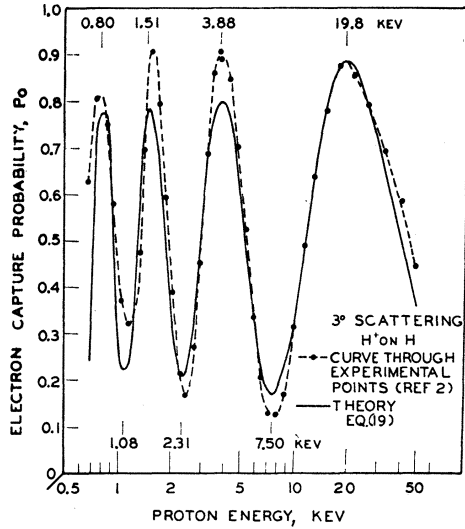


FIG. 1. The graph shows a comparison between theory and experiment for electron capture probability P_0 . An empirical curve was drawn by Lockwood and Everhart (Ref. 2) through their experimental points; it is reproduced here as the dashed line curve. The full line curve was calculated on the basis of Eq. (19). A first approximation was used in calculating the phase angle and damping factor appearing in that equation, as described in the text. The reference marks with numbers above and below the graph show the calculated maxima and minima.

where $\varphi_{1\pm}'$ is the first approximation quantity which satisfies Eq. (14). On substituting for g_{\pm}' from Eq. (15) and discarding the terms Φ_{\pm} for the reasons given earlier, we obtain

$$\begin{aligned}\Delta\varphi_+' &= \alpha V_{0eI} \exp(g_- - g_+) [\sin 2\varphi - i(1 - \cos 2\varphi)], \\ \Delta\varphi_-' &= \alpha V_{0eI} \exp(g_+ - g_-) [\sin 2\varphi + i(1 - \cos 2\varphi)].\end{aligned}\quad (23)$$

Integration gives

$$\begin{aligned}\operatorname{Re}(\Delta\varphi_+) &= \alpha \int V_{0eI} \sin 2\varphi \exp(g_- - g_+) dR, \\ \operatorname{Re}(\Delta\varphi_-) &= \alpha \int V_{0eI} \sin 2\varphi \exp(g_+ - g_-) dR.\end{aligned}\quad (24)$$

This second-order approximation to φ_{\pm} will introduce a correction in φ which, according to Eq. (16) and the equation preceding Eq. (19), is given by

$$\begin{aligned}\Delta\varphi &= \frac{1}{2}(\Delta\varphi_+ - \Delta\varphi_-) \\ &= \frac{1}{2}\alpha \int V_{0eI} \sin 2\varphi \\ &\quad \times [\exp(g_- - g_+) - \exp(g_+ - g_-)] dR.\end{aligned}\quad (25)$$

The imaginary part of $\Delta\varphi_{\pm}$ which results from integrating Eqs. (23) is, according to Eqs. (10) and (11),

equivalent to a correction in g_{\pm} . We may therefore write

$$\Delta g_+ = -\operatorname{Im}(\Delta\varphi_+) = 2\alpha \int V_{0eI} \sin^2 \varphi \exp(g_- - g_+) dR \quad (26)$$

$$\begin{aligned}\Delta g_- = -\operatorname{Im}(\Delta\varphi_-) &= -2\alpha \int V_{0eI} \sin^2 \varphi \\ &\quad \times \exp(g_+ - g_-) dR.\end{aligned}$$

3. DISCUSSION

The theoretical plot in Fig. 1, based on a first approximation to the solution of Eqs. (12) and (13), appears to be in good agreement with experiment, particularly with regard to the location in energy of the maxima and minima of P_0 . A second approximation calculation was made using Eqs. (25) and (26). The integrands in these equations were evaluated numerically using Eqs. (A4), (16), (A2), and (18) for values of the quantities V_{0eI} , φ , and g_{\pm} that appear in the integrands. Calculations for energies varying from 50 to 4 keV gave values for $\Delta\varphi$ varying between 0 and 0.1, while φ itself, in this energy interval, ranges from 0.63 to 4.9. This justifies confidence in the first approximation for φ as given by Eqs. (14) and (16). It also explains why the theoretical maxima and minima agree so closely with the experimental ones in Fig. 1, for their locations depend upon φ , as given by Eqs. (20) and (22). The corrections to g_{\pm} given by Eq. (26) were, however, in most cases equal to, or slightly larger than, g_{\pm} . For such cases we would need a third approximation correcting Eq. (15), due to Eq. (14) not holding in the second approximation. For energies above 35 keV the second approximation correction to g_{\pm} given by Eq. (26) is a safe improvement to the first approximation of g . The trend in such calculations is illustrated in Table I. For 34 keV the Δg_+ is about equal to g_+ . As the energy increases, Δg_{\pm} becomes smaller than g_{\pm} and the second approximation is valid; as the energy decreases below 34 keV, Δg_+ becomes larger than g_+ . This is reflected in the improvement of the second approximation over the first one for energies above 34 keV, and in the fact that for such energies $|F_0|^2 + |F_c|^2$ retains the value of 1 after the second approximation.

It should be noted that P_0 was calculated on the assumption that the electron will be only in the ground

TABLE I. Trend of 2nd approximation calculations based on the correction Δg_+ to the damping factor g_+ .

| E (keV) | Capture probability P_0 | | | | | |
|--------------|---------------------------|--------------|-------------|-------------|--------|---------------------|
| | g_+ | Δg_+ | 1st approx. | 2nd approx. | expt.* | $ F_0 ^2 + F_c ^2$ |
| 22.6 | -0.485 | 0.704 | 0.87 | 1.0 | 0.85 | 1.2 |
| 34.0 | -0.376 | 0.370 | 0.64 | 0.74 | 0.70 | 1.0 |
| 50.0 | -0.282 | 0.133 | 0.36 | 0.39 | 0.45 | 1.0 |

* Reference 2.

state of the target or scattered atom. In the experiment of Lockwood and Everhart² on H⁺-H collisions, P_0 was determined by measuring the fraction of neutral scattered particles to total scattered particles, without regard to states of excitation in the scattered or target systems. The favorable comparison of theory with experiment seems to indicate that the probability for capture with excitation is small. The method developed in the preceding section may be used to calculate this probability. In Appendix II we indicate how this may be done. The result for P_n , the relative probability for capture into an excited state ψ_n is given by Eq. (A17). The capture state ψ_n and the initial state ψ_0 are coupled together through a phase angle called ζ , which corresponds to φ for capture in the ground state. It can be seen from Eq. (A16) that ζ is very small since the orthogonality of ψ_0 and ψ_n makes V_{0nR} small. For the same reason V_{0n} and V_{cn} are small, leading to the result $\exp(p_+) \approx \exp(p_-)$. It then follows from Eq. (A17) that P_n is very small. This argument gets weaker as the energy decreases, due to the factor α in ζ .

The quantities φ and g_{\pm} that determine the magnitude of P_0 in Eq. (19) have no dependence on the scattering angle ϑ . The angle ϑ entered into the first one of Eqs. (3), but this would affect only the quantities Φ_{\pm} of Eqs. (12) and (13), and we concluded that these quantities give no significant contribution. Therefore we expect the curve of P_0 in Fig. 1 to be independent of scattering angle.

If we were to disregard the effect due to the change in the c.m., as represented by Eq. (4), the results would be considerably affected. Such an omission would have the effect of putting $k=0$ in the expression for V_{0c} , Eq. (6b). This in turn would make $\tilde{k}=0$ in Eq. (21) and would shift the resonances and antiresonances in the theoretical curve of Fig. 1 in the following manner: The resonances at 19.8 and 3.88 keV would be shifted to 40.5 and 4.5 keV, respectively. The antiresonances at 7.50 and 2.3 keV would be shifted to 10.2 and 2.5 keV, respectively. Such shifts would materially reduce the agreement with experiment. A more drastic effect of disregarding the c.m. correction results in making V_{0cI} , Eq. (A2a), equal to zero. This would make $\exp(g_{\pm})=1$ and would result in the disappearance of damping. The P_0 curve of Fig. 1 would then oscillate between maxima and minima of 1 and 0. As it turned out in this problem the damping of the resonances and antiresonances is a sensitive part of the theory. While the location in energy of the maxima and minima is given directly by the first approximation, the factors $\exp(g_{\pm})$ which determine the damping require several approximations and depend critically on the potential.

APPENDIX I: EVALUATION OF THE QUANTITY $V_{0c}(R)$

To evaluate $V_{0c}(R)$ it is convenient to use elliptic coordinates. We place the origin O of the electron co-

ordinates midway between the two nuclei, designate the internuclear distance R by $2a$, and let the z axis be along \mathbf{R} . The elliptic coordinates ξ, η, φ , of the electron are defined as follows:

$$\xi = (r_1 + r_2)/2a; \quad \eta = (r_1 - r_2)/2a; \\ \text{and } \varphi \text{ is the azimuthal angle.}$$

As before, the distances of the electron from nuclei 1 and 2 are designated by r_1 and r_2 . The volume element is

$$d\tau = a^3(\xi^2 - \eta^2)d\xi d\eta d\varphi.$$

A further useful relation is $z = a\xi\eta$. The normalized ground-state wave functions for the electron are, in atomic units,

$$\psi_0(r_1) = 2 \exp(-r_1)/(4\pi)^{1/2}; \\ \psi_0(r_2) = 2 \exp(-r_2)/(4\pi)^{1/2}.$$

Referring to Eq. (6b) and using elliptic coordinates, we obtain, after integrating over φ ,

$$V_{0c}(R) = \frac{1}{2}R^2 \int_{-1}^{+1} d\eta \int_1^{\infty} \exp[-R\xi(1-ik\eta)] \xi d\xi \\ - \frac{1}{2}R^2 \int_{-1}^{+1} d\eta \int_1^{\infty} \exp[-R\xi(1-ik\eta)] \eta d\xi. \quad (\text{A1})$$

Integration gives a real result for the first term on the right and an imaginary result for the second term. In accordance with our notation earlier, we call the first term $V_{0cR}(R)$ and the second term (excluding the negative sign) $V_{0cI}(R)$. The first term is integrated simply, giving

$$V_{0cR}(R) = \frac{e^{-R}(\sin kR + k \cos kR)}{k(1+k^2)} \quad (\text{A2})$$

and

$$V_{0cI}(R) = \int_0^{\infty} V_{0cR}(R) dR = 2/(1+k^2)^2. \quad (\text{A3})$$

The second term may be first integrated over η , and after a partial integration over ξ we arrive at the expression

$$V_{0cI}(R) = \frac{e^{-R} \sin kR}{k^2} - \frac{R}{k^2} \int_R^{\infty} e^{-x} \frac{\sin kx}{x} dx. \quad (\text{A2a})$$

The integral on the right can be evaluated by expanding $\sin kx$ as a series in powers of x and then integrating each term. This leads to the following result:

$$V_{0cI}(R) = e^{-R} [\sin kR - RS(k, R)]/k^2, \\ S(k, R) = \sum_{n=0}^{\infty} (-)^n \frac{k^{2n+1}}{(2n+1)} \nu(2n), \\ \nu(2n) = \sum_{s=0}^{2n} \frac{R^s}{s!}. \quad (\text{A4})$$

It can easily be shown, either by this series or by working directly with the second term on the right of Eq. (A1), that

$$\int_0^{\infty} V_{0cI}(R)dR = k/(1+k^2)^2. \quad (\text{A5})$$

APPENDIX II: DERIVATION OF A FORMULA FOR THE PROBABILITY OF CAPTURE INTO AN EXCITED STATE

Let us consider an excited state ψ_n in the scattered atom. If we denote its scattering amplitude by $f_n(R')$, we write, in place of Eq. (2),

$$\Psi = F_0(R')\psi_0(r_1) + F_c(R')\psi_0(r_2) + f_n(R')\psi_n(r_2), \quad (\text{A6})$$

and in place of Eqs. (5) and (7) we write

$$(\nabla^2 + K^2 - 2\alpha KR^{-1})F_0 + 2\alpha K(V_{00}F_0 + V_{0c}F_c + V_{0n}f_n) = 0, \quad (\text{A7})$$

$$(\nabla^2 + K^2 - 2\alpha KR^{-1})f_n + 2\alpha K(W_{nn}f_n + V_{0n}^*F_0 + V_{cn}F_c) = 0, \quad (\text{A8})$$

$$V_{0n} = \int r_1^{-1} \psi_0(r_1) \psi_n(r_2) \exp[ik(\mathbf{r}_1 + \mathbf{r}_2) \cdot \hat{\mathbf{R}}] d\mathbf{r}_1$$

$$V_{cn} = \int r_1^{-1} \psi_0(r_2) \psi_n^*(r_2) d\mathbf{r}_2, \quad (\text{A9})$$

$$W_{nn} = V_{nn} + E_0 - E_n$$

$$V_{nn} = \int r_1^{-1} |\psi_n(r_2)|^2 d\mathbf{r}_2,$$

where E_0 and E_n are the energies of the ground and excited states, respectively. By adding and subtracting Eqs. (A7) and (A8) we obtain, in analogy to Eqs. (8a) and (8b), the following coupled equations:

$$(\nabla^2 + K^2 - 2\alpha KR^{-1})(F_0 + f_n) + 2\alpha KU = 0$$

$$(\nabla^2 + K^2 - 2\alpha KR^{-1})(F_0 - f_n) + 2\alpha KT = 0$$

$$U = [\frac{1}{2}(V_{00} + W_{nn}) + V_{0nR}](F_0 + f_n) + [\frac{1}{2}(V_{00} - W_{nn}) + iV_{0nI}](F_0 - f_n) + (V_{0c} + V_{cn})F_c \quad (\text{A10})$$

$$T = [\frac{1}{2}(V_{00} + W_{nn}) - V_{0nR}](F_0 - f_n) + [\frac{1}{2}(V_{00} - W_{nn}) - iV_{0nI}](F_0 + f_n) + (V_{0c} - V_{cn})F_c$$

$$V_{0nR} \equiv \text{Re}(V_{0n}); \quad V_{0nI} \equiv \text{Im}(V_{0n}^*).$$

As we did in Eqs. (10) and (11), we assume solutions

of the form

$$F_0 + f_n = \frac{1}{2}I + \frac{1}{2}Sf(\vartheta) \exp(i\zeta_+ + p_+) \quad (\text{A11})$$

$$F_0 - f_n = \frac{1}{2}I + \frac{1}{2}Sf(\vartheta) \exp(i\zeta_- + p_-).$$

On substituting these solutions into Eqs. (A10), and following the procedure that led to Eqs. (12) and (13), we obtain the following differential equations:

$$-\zeta_+' + ip_+' + \alpha[\frac{1}{2}(V_{00} + W_{nn}) + V_{0nR}] \times \exp(i\zeta_+ + p_+) + i\alpha V_{0nI} \exp(i\zeta_- + p_-) + X = 0,$$

$$-\zeta_-' + ip_-' + \alpha[\frac{1}{2}(V_{00} + W_{nn}) - V_{0nR}] \times \exp(i\zeta_- + p_-) - i\alpha V_{0nI} \exp(i\zeta_+ + p_+) + Y = 0, \quad (\text{A12})$$

$$X = \frac{1}{2}(V_{00} - W_{nn}) \exp(i\zeta_- + p_-) + (V_{0c} + V_{cn})F_c/[Sf(\vartheta)],$$

$$Y = \frac{1}{2}(V_{00} - W_{nn}) \exp(i\zeta_+ + p_+) + (V_{0c} - V_{cn})F_c/[Sf(\vartheta)].$$

Apart from the terms X and Y , Eq. (A12) has the same appearance as Eqs. (12) and (13). By the same reasoning that led to Eqs. (14) and (15) we take as a first approximation,

$$-\zeta_{\pm}' + \alpha[\frac{1}{2}(V_{00} + W_{nn}) \pm V_{0nR}] = 0 \quad (\text{A13})$$

$$p_+' \exp(p_+) + \alpha V_{0nI} \exp(p_-) + \text{Im}(X)/\cos\zeta = 0, \quad (\text{A14})$$

$$p_-' \exp(p_-) - \alpha V_{0nI} \exp(p_+) + \text{Im}(Y)/\cos\zeta = 0. \quad (\text{A15})$$

The solution to Eq. (A13) is

$$\zeta_{\pm} = \zeta_0 \pm \zeta,$$

$$\zeta_0 = \alpha \int_0^R \frac{1}{2}(V_{00} + W_{nn}) dR, \quad (\text{A16})$$

$$\zeta = \alpha \int_0^R V_{0nR} dR.$$

The integration of Eqs. (A14) and (A15) can be simplified by noting that V_{0n} and V_{cn} are small, and therefore $\exp(p_+) \approx \exp(p_-)$. The value of F_c is known, being given by Eqs. (10) and (11). In the same manner that we arrived at Eq. (19), we obtain for the relative probability P_n for capture into the state n ,

$$P_n = \frac{1}{4} \{ \cos^2\zeta [\exp(p_+) - \exp(p_-)]^2 + \sin^2\zeta [\exp(p_+) + \exp(p_-)]^2 \}, \quad (\text{A17})$$

since f_n is small compared to F_0 and F_c .

The problem of finding the probability for the scattering of the ion with the target atom being left in a certain excited state can be treated by this method. One would then let ψ_n be an excited state in the target atom and derive the corresponding matrix elements.