Single-electron capture by slow protons in helium

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Single-electron capture by slow protons in helium

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Abstract. The perturbed stationary state method is applied to

$$He(1s^2) + H^+ \rightarrow He^+(1s) + H(1s)$$

but with neglect of momentum transfer. The calculations of Green *et al.* and of Sin Fai Lam show that the approximation is certainly untenable at energies above 16 kev. The experimental results of Hasted and Stedeford and of Stier and Barnett for the sum total of all processes involving charge transfer from helium to protons are exceeded from 3 to 10 kev. The differential cross section at small angles of deflection compares reasonably well with the experiments of Helbig and Everhart for energies below 5 kev.

1. Introduction

Bates and McCarroll (1958, 1962) removed some defects in the perturbed stationary state method for charge transfer in slow atom–ion collisions by allowing for the momentum of the captured electron, and obtained results independent of the choice of origin. To extend this to the case when more than one electron is available is difficult, except in the limiting case when the velocity of encounter approaches zero, and because of this difficulty the present calculations allow for no momentum transfer at all.

An impact parameter treatment will be adopted; that this is essentially equivalent to a full quantal treatment has been demonstrated by several authors (Crothers and Holt 1966, McCarroll and Salin 1966).

2. Notation and basic equations

For a collision involving two atomic nuclei A and B, of charges z_A and z_B, and two electrons P_1 and P_2, we choose an origin at an arbitrary position O in AB so that $\overrightarrow{OA} = -p\boldsymbol{R}$, $\overrightarrow{OB} = q\boldsymbol{R}$ with $p+q = 1$. Let $\overrightarrow{AP}_\alpha = \boldsymbol{r}_\alpha$, $\overrightarrow{BP}_\alpha = \boldsymbol{s}_\alpha$ and $\overrightarrow{OP}_\alpha = \boldsymbol{\rho}_\alpha$ ($\alpha = 1, 2$). Following the usual assumption that $\boldsymbol{v} = \mathrm{d}\boldsymbol{R}/\mathrm{d}t$ is constant, let P denote the impact parameter and write $R^2 = P^2 + Z^2$ so that $Z = vt$.

The (normalized) eigenfunctions ϕ_n and energies ϵ_n of the quasi-molecule AB+2e at nuclear separation R are given by

$$H\phi_n = \epsilon_n \phi_n \tag{1}$$

where

$$H = -\tfrac{1}{2}\nabla^2_{\rho_1\rho_2 R} - \tfrac{1}{2}\nabla^2_{\rho_2\rho_1 R} - \frac{z_A}{r_1} - \frac{z_B}{s_1} - \frac{z_A}{r_2} - \frac{z_B}{s_2} + \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}. \tag{2}$$

Suppose initially ($t = -\infty$, $R = \infty$) both electrons are bound to A in a molecular state denoted by $\phi_i^{AA}(-\infty)$ and consider the amplitude for the transition

$$A^{(z_A-2)(+)} + B^{z_B(+)} \rightarrow A^{(z_A-1)(+)} + B^{(z_B-1)(+)} \tag{3}$$

to a final state

$$\phi_f^{AB/BA}(t) = (\phi_f^{AB} \pm \phi_f^{BA}) \exp\left\{-\mathrm{i}\int^t \epsilon_f(R)\,\mathrm{d}t\right\}, \qquad (t \rightarrow \infty)$$

where ϕ_f^{BA} results from interchanging the coordinates of the electrons in ϕ_f^{AB}, the plus sign being taken for a singlet state and the minus for a triplet. This transition amplitude is calculated by expanding the solution of the full Schrödinger equation

$$\left(H - \mathrm{i}\boldsymbol{v}\,.\,\nabla_{R_{\rho_1\rho_2}} - \mathrm{i}\frac{\partial}{\partial t_{\rho_1\rho_2 R}}\right)\Psi = 0 \tag{4}$$

in terms of the complete set $\phi_n(t)$ modified to allow for momentum transfer of the captured electron (Bates and McCarroll 1958, 1962).

The modified initial state eigenfunction is

$$\Phi_i = \phi_i^{AA} \exp\left\{-ip\boldsymbol{v}\cdot(\boldsymbol{\rho}_1+\boldsymbol{\rho}_2) - i\int^t \epsilon_i(R)\,dt - ip^2v^2t\right\}. \tag{5a}$$

To preserve symmetry and normalization the momentum transfer factors in the final state must be inserted in a more complicated way:

$$\Phi_f = N_f(R)[\phi_f^{AB}\exp\{i\boldsymbol{v}\cdot(-p\boldsymbol{\rho}_1+q\boldsymbol{\rho}_2)\} \pm \phi_f^{BA}\exp\{i\boldsymbol{v}\cdot(-p\boldsymbol{\rho}_2+q\boldsymbol{\rho}_1)\}]$$
$$\times \exp\left\{-i\int^t \epsilon_f(R)\,dt - \tfrac{1}{2}i(p^2+q^2)v^2t\right\} \tag{5b}$$

where $|N_f(R)|$ approaches unity at low velocities or at large nuclear separations.

If we make the two-state approximation and substitute

$$\Psi = a(P, Z)\Phi_i + b(P, Z)\Phi_f \tag{6}$$

into (4) taking suitable scalar products, the resulting equations for $a(P, Z)$ and $b(P, Z)$ are very cumbersome. However, as $v \to 0$ they assume the form

$$\frac{da}{dZ} - bL_{fi}\exp\left\{\frac{i}{v}\int_{-Z}^{Z}(\epsilon_i-\epsilon_f)\,dZ\right\} = 0 \tag{7a}$$

$$\frac{db}{dZ} + a\bar{L}_{fi}\exp\left\{-\frac{i}{v}\int_{-Z}^{Z}(\epsilon_i-\epsilon_f)\,dZ\right\} = 0 \tag{7b}$$

where Z_0 is such that the interaction may be neglected for $|Z| > Z_0$ and

$$L_{fi} = (\phi_f, \partial\phi_i/\partial Z_{r_1r_2}) \tag{8}$$

$\bar{L}_{fi}$ being the complex conjugate.

In the absence of momentum factors in (5*a*) and (5*b*) equations (7*a*) and (7*b*) would be obtained but with the differentiation in (8) depending arbitrarily on the choice of origin.

3. Electron capture by slow protons in helium

The simplest example of asymmetric charge transfer involving two electrons as described in (3) is the σ–σ transition

$$He(1s^2) + H^+ \to He^+(1s) + H(1s) + 11 \text{ ev}. \tag{9}$$

Green *et al.* (1965) and Sin Fai Lam (1967) have calculated cross sections for a range of energies exceeding 1 kev. The perturbed stationary state method is suitable for an overlapping range extending to the lowest energies. The only previous perturbed stationary state calculations for (9) known to the authors are those of Massey and Smith (1933) and Haywood (1959). Rosentsveig and Gerasimanko (1955) have treated double capture by protons in helium, and recently Matsuzawa (1967) has performed a perturbed stationary state calculation for α-particles in hydrogen.

3.1. *Calculation of molecular eigenfunctions and the matrix element* L_{fi}

Variational functions for the present calculation were chosen of the form

$$\phi_n(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{R}) = \lambda_n(R)\phi_n^{(1)} + \mu_n(R)\phi_n^{(2)} \tag{10}$$

with

$$\phi_n^{(1)} = \phi_{H+He^+} = \chi_n^A(\boldsymbol{r}_1)\chi^B(\boldsymbol{s}_2) + \chi_n^A(\boldsymbol{r}_2)\chi_n^B(\boldsymbol{s}_1)$$
$$\phi_n^{(2)} = \phi_{H^-+He} = \chi_n^{A'}(\boldsymbol{r}_1)\chi_n^{A''}(\boldsymbol{r}_2) + \chi_n^{A''}(\boldsymbol{r}_1)\chi_n^{A'}(\boldsymbol{r}_2)$$
$$\chi_n^A(\boldsymbol{r}) = \exp\{-g_n(R)r\}, \qquad \chi_n^B(\boldsymbol{s}) = \exp\{-k_n(R)s\}$$
$$\chi_n^{A'}(\boldsymbol{r}) = \chi_n^{A''}(\boldsymbol{r}) = \exp\{-h_n(R)r\} \qquad (n = i, f).$$

The energy levels $\epsilon_n(R)$ for the two lowest states of HeH^+ are given by

$$|H_{jk}-\epsilon S_{jk}| = 0 \tag{11}$$

where

$$H_{jk} = H_{kj} = (\phi^{(j)}, H\phi^{(k)})$$

$$S_{jk} = S_{kj} = (\phi^{(j)}, \phi^{(k)}) \qquad (j, k = 1, 2)$$

and the corresponding values of $x = \lambda/\mu$ are given by

$$(H_{12}S_{22}-H_{22}S_{12})x^2+(H_{11}S_{22}-H_{22}S_{11})x+H_{11}S_{12}-H_{12}S_{11} = 0. \tag{12}$$

If the orbital parameters g, h, k are fixed, we obtain from (12) approximate molecular eigenfunctions which are *orthogonal* and represent the two sides of (9) in the separated atom limit. When the parameters are varied in such a way that the two roots of (11) are independently minimized we again find the correct eigenfunctions at infinite nuclear separation (within the limitations imposed by the form of $\phi_n^{(2)}$), and improved functions at finite separation although strict orthogonality has been sacrificed. The largest value of (ϕ_i, ϕ_f) was found to be 0·02 at $R = 0{\cdot}44$ and to within about 1% the energies $\epsilon_n(R)$ agree with the more elaborate calculations of Michels (1966). A further check is provided by the spectroscopic values of the two lowest energies of Li^+: Moore (1949) gives $-7{\cdot}34$ and $-5{\cdot}11$ atomic units, and the above procedure yields $-7{\cdot}25$ and $-5{\cdot}02$ in the united atom limit.

Wave functions of this form using bipolar coordinates are convenient for the perturbed stationary state method. For a σ–σ transition we may calculate the derivative needed in L_{fi} from

$$\frac{\partial}{\partial Z_{r_1r_2}}\phi_i = \frac{Z}{R}\frac{\partial'}{\partial R_{r_1r_2}}\phi_i$$

where the prime indicates that $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ are held constant in the rotating frame with AB as polar axis. Then

$$\frac{\partial'}{\partial R_{r_1r_2}} = \frac{\partial}{\partial R}+\frac{1}{2Rs_1}(R^2+s_1{}^2-r_1{}^2)\frac{\partial}{\partial s_1}+\frac{1}{2Rs_2}(R^2+s_2{}^2-r_2{}^2)\frac{\partial}{\partial s_2}.$$

This yields a lengthy formula for L_{fi} (Colegrave 1964).

3.2. *Solution of the coupled equations for* $b(P, \infty)$

(7*a*) and (7*b*) give four first-order coupled equations for the real and imaginary parts of $a(P, Z)$ and $b(P, Z)$ and these are solved for the final transition amplitude $b(P, Z_0)$ subject to the initial conditions $a(P, -Z_0) = 1$ and $b(P, -Z_0) = 0$. The structure of the equations is such that this exit value of b is purely imaginary. Z_0 was put equal to 10 atomic units and a programme based on the Runge–Kutta method was used to solve the coupled equations. Values of L_{fi}, ϵ_f and ϵ_i were interpolated from 120 directly calculated values.

With the approximation $a(P, Z) = 1$ throughout, the encounter equations (7) may be solved by quadrature (cf. Haywood 1959) and this reproduces almost exactly the values of $b(P, Z_0)$ found by solving the coupled equations, the only difference being for small impact parameters when larger values of $b(P, Z_0)$ are found. A difference of only a few per cent occurs in the total cross sections even for energies as high as 25 kev.

Calculations using cruder wave functions with fixed orbital parameters indicate that the transition probabilities do not depend very crucially on the wave functions.

4. Comparison with other calculations and with experiment

Some of the computed probability amplitudes $ib(P, Z_0)$ are shown in figure 1, and the cross section is shown in figure 2 where it is compared with experiments (Hasted and Stedeford 1955, Stier and Barnett 1956, Allison 1958) for the total charge transfer from

helium to protons, and also with the calculations of Green *et al.* (1965) and of Sin Fai Lam (1967). The latter author uses a four-state approximation and the calculations indicate that process (9) accounts for almost all the charge transfer for energies with which we are concerned above 1 kev.

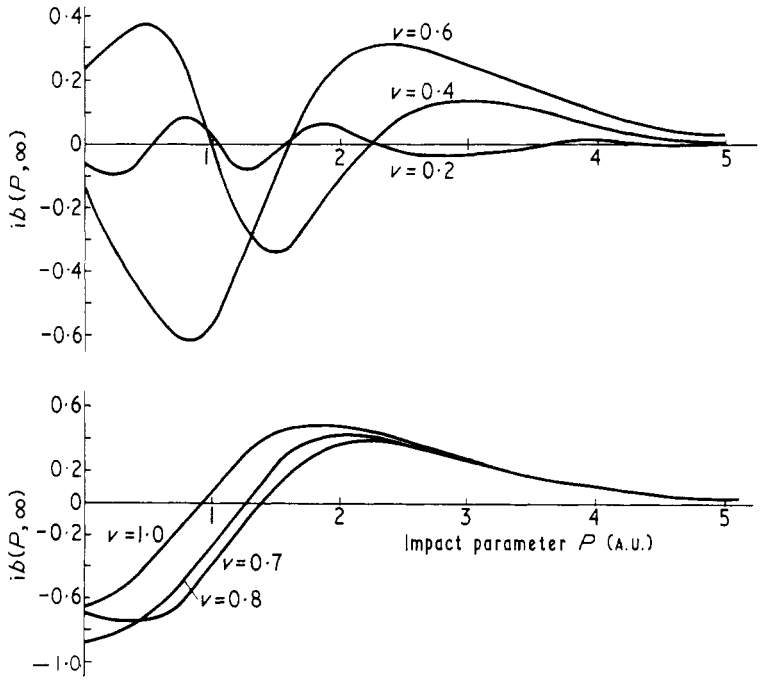

Figure 1. Probability amplitude for electron capture by protons from helium. $ib(P, \infty)$ plotted against impact parameter P for v = 0·2, 0·4, 0·6, 0·7, 0·8, 1·0 A.U. (1, 4, 9, 12·25, 16, 25 kev).

The cross section as calculated by the present method appears to be overestimated by a factor of up to 25% in the energy range 4–10 kev. This is in accord with the prediction of Bates and McCarroll (1958) that neglecting momentum transfer increases the cross section. The maximum value of the cross section is rather low when we compare it with experiment (1·7 instead of 2·2 πa_0^2). The energy at which this occurs agrees quite well with the experimental value of 25 kev, although the actual peak is much too broad, presumably owing to a rapid deterioration in the approximation in this region. At higher energies the present results are very poor when compared with experiment or high-energy calculations (Mapleton 1961, 1963).

The experiments of Helbig and Everhart (1964) on close encounters provide an independent comparison with experiment. Assuming an elastic collision, the connection between the angle of deflection θ and the impact parameter P is given by the classical formula

$$\theta = \pi - 2\int_{R_0}^{\infty} \frac{\mathrm{d}R}{R[R^2\{1-V(R)/E\}/P^2-1]^{1/2}}$$

where $V(R) = Z/R$, $Z = 1{\cdot}6875$, $E = \frac{1}{2}Mv^2$, M being the reduced mass of the helium–proton system and R_0 the perihelion distance. This reduces to

$$\theta = \pi - 2P\int_0^{\infty} \frac{\mathrm{d}u}{a\cosh u + Z/2E} \tag{13}$$

where $a^2 = P^2 + Z^2/4E^2$.

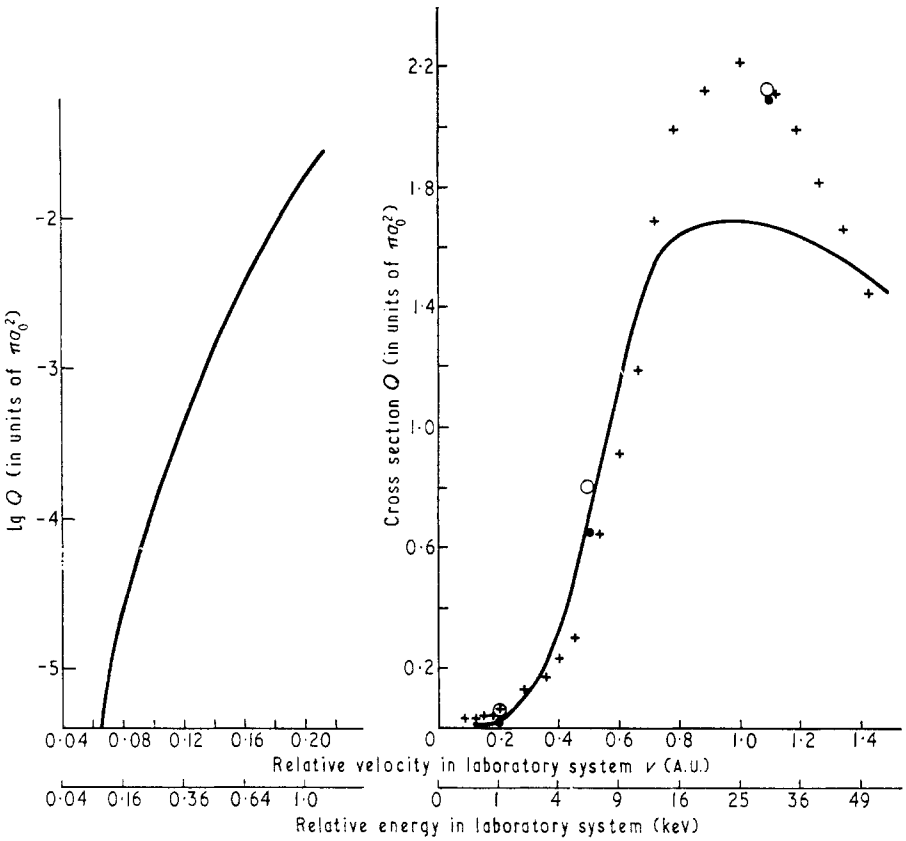

Figure 2. Cross sections for electron capture by protons from helium plotted against relative velocity v (A.U.), or incident proton energies in kev: calculations for $He(1s^2)+H^+ \rightarrow He^+(1s)+H(1s)$ compared with the experimental values of Hasted and Stedeford and with the calculations of Green *et al.* and of Sin Fai Lam. —— present calculations; + experiment; ● Green *et al.* 1965; ○ Sin Fai Lam 1967.

The connection between θ and P at various energies is shown in table 1.

Table 1

P	1 kev $v = 0{\cdot}2$	2·25 kev $v = 0{\cdot}3$	4 kev $v = 0{\cdot}4$	6·25 kev $v = 0{\cdot}5$	25 kev $v = 1$
0·1	32·06	14·56	8·22	5·27	1·33
0·2	16·35	7·31	4·12	2·64	0·668
0·4	8·22	3·67	2·07	1·33	0·339
0·6	5·49	2·45	1·38	0·888	0·230
0·8	4·12	1·84	1·04	0·669	0·175
1·0	3·30	1·47	0·833	0·537	0·142
1·2	2·75	1·23	0·696	0·449	0·120
1·4	2·36	1·06	0·598	0·386	0·104
1·6	2·07	0·925	0·525	0·339	0·093
1·8	1·84	0·823	0·467	0·303	0·083
2·0	1·66	0·742	0·422	0·274	0·076
3·0	1·11	0·498	0·285	0·186	0·054
4·0	0·833	0·376	0·216	0·142	0·043
5·0	0·669	0·303	0·175	0·116	0·037

Figure 3 shows the capture probability plotted against energy for encounters at two of the angles of deflection used by Helbig and Everhart. The agreement is reasonable at energies lower than about 5 kev. Some of the deviation may be due to the inadequacy of

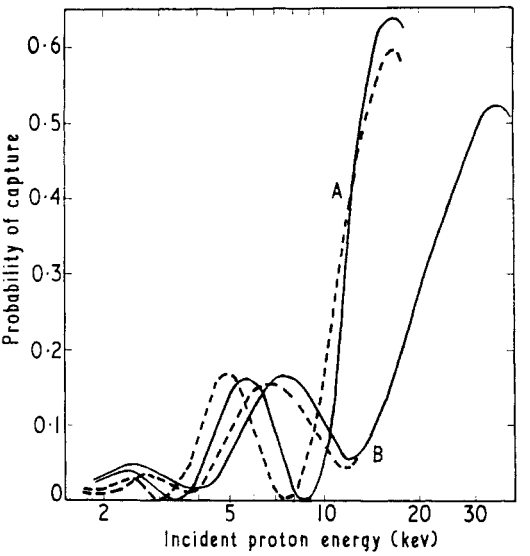

Figure 3. Probability of electron capture from helium by protons of relative velocity v (A.U.) at small angles of deflection. Curves A, using present calculations and classical orbit; curves B, experimental results of Helbig and Everhart (1964). – – – – 1·5°, ——— 3°.

formula (13), but from the analysis of Bates *et al.* (1953) it looks as if the assumption of an elastic collision, in the sense of no discontinuity in the classical orbit, is equivalent to the usual assumption of constant relative velocity v in the perturbed stationary state method.

5. Discussion

For a range of energies above 4 kev ($v = 0{\cdot}4$) figures 2 and 3 show that the transition probability given by equations (7) is on the whole too large. As remarked in the previous section, this is to be expected with neglect of momentum transfer. The situation may be a little better than it appears from figure 2, since the experimental points can hardly be said to follow a smooth curve at the lower energies when, of course, the experimental conditions become increasingly difficult. At about 16 kev the cross section flattens out too rapidly and we may assume that the approximation is beginning to fail badly.

No calculated probabilities were found to exceed unity as in the calculations of Haywood (1959) where an unsymmetrized final state wave function was used.

From figure 2 we see an activation energy at about 100 ev in agreement with the early calculations of Massey and Smith (1933) who, however, obtained much larger cross sections at low energies. There is good agreement with the results of Green *et al.* (in which momentum transfer is included) at 1 and 8 kev. Sin Fai Lam includes momentum transfer and more channels and is in agreement at the higher, but not at the lower, energies in this range. At 1 kev Sin Fai Lam obtains three times the cross section of Green *et al.* and agrees with the experimental value (see figure 2). This raises the question of whether the present calculations are too low at very low energies (100 ev–1 kev) where they are only about 25% of the few experimental values, but where we should expect the perturbed stationary state method to give good results. The same situation of cross sections much lower than the experimental values at low energies and a too rapid increase with incident energy has been found by Matsuzawa (1967) using the perturbed stationary state method

(with neglect of momentum transfer) for electron capture by α-particles in hydrogen. It may well be that channels other than those considered by Sin Fai Lam are important at very low energies.

We may conclude that the present calculations are a reasonably good estimate of the total charge transfer from helium to protons in the energy range 1–16 kev, but at the lower energies in this range the approximation of neglecting the momentum transferred by the captured electron causes a too rapid increase in the cross section resulting in an overestimate by a factor of up to 25%. At energies higher than 16 kev the approximation breaks down completely. Below 1 kev the calculations should be reliable for process (9), but there is some doubt whether this channel is the only one that is important for electron capture at these low energies.

The neglect of back-coupling, i.e. the approximation $a(P, Z) = 1$, appears to be less serious than that of momentum transfer.

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