Sum Rules for Hydrogenic Wave Functions, with Applications to Charge-Exchange and Ionization Processes

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We prove some general addition theorems for certain matrix elements which involve hydrogen-atom wave functions. In particular, if $f_{nlm}(\mathbf{q})$ is the Fourier transform of the hydrogen-atom wave function with quantum numbers n,l,m, then $|f_{nlm}(\mathbf{q})|^2$ summed over all l and m for a given n is equal to $2^6\pi a_0^{-5}n^{-3}\times(q^2+a_0^{-2}n^{-2})^{-4}$, where a_0 is the Bohr radius. Two applications of the theorems are given. Firstly, we consider charge-exchange reactions of the type $H^+ + H(n_1l_1m_1) \rightarrow H(n_2l_2m_2)+H^+$ and use our general theorems to obtain for the cross section for reactions proceeding from the initial atomic state n_1 to the final state n_2 an expression which is both simple and fully exact (in Born approximation). Secondly, we indicate how the theorems may be applied to get simple expressions for the cross sections for ionization of excited hydrogen atoms by various processes.

1. INTRODUCTION

In this paper we consider some addition theorems for the Fourier transform of the simple H-atom wave function ϕ_{nlm},

$$f_{nlm}(\mathbf{q})\equiv\int d\mathbf{r}\phi_{nlm}(\mathbf{r})\exp(i\mathbf{q}\cdot\mathbf{r}), \qquad (1)$$

where n, l, m are the usual H-atom quantum numbers. Such expressions do not often occur in physical contexts, matrix elements containing two atomic wave functions being more frequently met. However, (1), and the related function $g(\mathbf{q})$ defined below, can occur as the matrix elements in charge-exchange problems, and in expressions for cross sections for ionizing excited H atoms.

In Sec. 2 we prove the following useful theorem:

$$\sum_{l=0}^{n-1}\sum_{m=-l}^{l}|f_{nlm}(\mathbf{q})|^2=\frac{2^6\pi\lambda^5}{n^3}\frac{1}{(q^2+\lambda^2n^{-2})^4} \qquad (2)$$

(λ is the inverse of the Bohr radius). Physically, the simplicity of this and allied results may be expected from the remark that the wave functions $\phi_{nlm}(\mathbf{r})$ form a complete set with respect to square integrable functions[1] (although in Hilbert space one must add to $\{\phi_{nlm}\}$ the free-electron Coulomb wave functions to complete the set). It is then reasonable to expect that the angular part of the completeness (which is the part involved in summing over l and m) will lead from the left-hand side of Eq. (2) to a simple expression in n and q. The rigorous proof in Sec. 2 follows these lines.

Equation (2) is a special case of a more general relation which may be proved for

$$\sum_{l=0}^{n-1}\sum_{m=-l}^{l}f_{nlm}(\mathbf{q})f_{nlm}^*(\mathbf{q}'). \qquad (3)$$

This more general result [see Eq. (24)] can be expressed in terms of Tschebyscheff polynomials. Results such as (2) for functions like $|f_{nlm}(\mathbf{q})|^2$ summed over l and m are useful in evaluating cross sections, while results for the summand $|f_{nlm}(\mathbf{q})f_{nlm}(\mathbf{q}')|$ serve in the evaluation of transition probabilities for individual impact parameters.[2]

Results for the sum over the quantum numbers m only ($m=-l$ to $+l$) for the summand $|f(\mathbf{q})f(\mathbf{q}')|$ and the special case $|f(\mathbf{q})|^2$ are also obtained en route in Sec. 2.

The above discussion, and that in Sec. 2, have been given for the Fourier transform of the H-atom wave functions, $f_{nlm}(\mathbf{q})$: in Sec. 3 we show how any expression for $f(\mathbf{q})$ can be trivially converted into an expression for the matrix element

$$g_{nlm}(\mathbf{q})\equiv\int\frac{d\mathbf{r}}{r}\phi_{nlm}(\mathbf{r})\exp(i\mathbf{q}\cdot\mathbf{r}) \qquad (4)$$

by use of the relationship (28). For example, use of (28) gives immediately,

$$\sum_{l=0}^{n-1}\sum_{m=-l}^{l}|g_{nlm}(\mathbf{q})|^2=\frac{2^4\pi\lambda^3}{n^3}\frac{1}{(q^2+\lambda^2n^{-2})^2}. \qquad (5)$$

The matrix elements $f(\mathbf{q})$ and $g(\mathbf{q})$ are the only ones of interest in the physical contexts which prompted the present investigation: however the technique used in Sec. 3 to relate $f(\mathbf{q})$ and $g(\mathbf{q})$ can be extended to generate other related matrix elements, for which the analogs of Eqs. (2) and (24) can then be obtained.

In Sec. 4 we outline two applications of the addition theorems.

Firstly we consider charge-exchange reactions of the type

$$H^+ + H(n_1l_1m_1) \rightarrow H(n_2l_2m_2)+H^+. \qquad (6)$$

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[1] See, for example, R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience Publishers, Inc., New York, 1953), Vol. I, p. 95.

[2] The sum over all impact parameters which leads from individual transition probabilities to total cross sections introduces a factor $\delta(\mathbf{q}-\mathbf{q}')$.

We sum over the final-state quantum numbers l_2 and m_2, and average over the initial quantum numbers l_1 and m_1, to get the total cross section for reactions proceeding from the initial atomic state n_1 to the final state n_2:

$$\sigma(\langle n_1\rangle|n_2) = \frac{1}{n_1^2}\sum_{l_1=0}^{n_1-1}\sum_{m_1=-l_1}^{l_1}\sum_{l_2=0}^{n_2-1}\sum_{m_2=-l_2}^{l_2}\sigma(n_1l_1m_1|n_2l_2m_2). \quad (7)$$

(n_1^2 is the total degeneracy of the state with principal quantum number n_1.) The resultant simple expression (37) for $\sigma(\langle n_1\rangle|n_2)$ is fully *exact* in Born approximation. Previous work in this field comprises calculations of $\sigma(1|n_2l_2)$ for $n_2\leqslant 4$ [3] and approximate results for $n_2\gg 1$,[4–7] together with numerical calculations of $\sigma(20|n_20)$ and $\sigma(60|n_20)$ for all n_2.[8] [There is, of course, extensive work on the special case of $1s$–$1s$ transitions, $\sigma(1|1)$.]

As a second application, we consider the ionization of H atoms by various mechanisms, namely collisions with massive particles (ions and atoms) and photoelectric ionization (again in Born approximation). The cross sections for such processes contain matrix elements of the form (1). Particularly when the H atom to be ionized is in a highly excited state, the present theorems are seen to lead to simple expressions for the cross sections.

2. THEOREMS ON $f_{nlm}(\mathbf{q})$

We now proceed to evaluate the sums over m, and over l and m, of the function $f_{nlm}(\mathbf{q})f_{nlm}^*(\mathbf{q}')$.

We begin by writing down the wave functions for the simple H atom:

$$\phi_{nlm}(\mathbf{r})=R_{nl}(r)Y_{lm}(\theta,\phi)\,, \quad (7)$$

$$R_{nl}(r)=\frac{2\lambda^{3/2}}{n^2}\left\{\frac{(n-l-1)!}{(n+l)!}\right\}^{1/2}\frac{x^le^{-x/2}}{(n+l)!}L_{n-l-1}^{2l+1}(x)\,, \quad (8)$$

where for convenience x is defined by

$$x\equiv 2\lambda r/n. \quad (9)$$

λ is the inverse Bohr radius, $\lambda=1/a_0=me^2/\hbar^2$, and the Laguerre polynomials are defined by the generating function

$$\frac{\exp(-xt/(1-t))}{(1-t)^{2l+2}}=\sum_{i=0}^{\infty}\frac{t^iL_i^{2l+1}(x)}{(i+2l+1)!}. \quad (10)$$

We then use the standard expansion

$$\exp(i\mathbf{q}\cdot\mathbf{r})=\sum_{l=0}^{\infty}i^l(2l+1)j_l(qr)P_l(\cos\vartheta) \quad (11)$$

together with the addition theorem for spherical harmonics,

$$(2l+1)P_l(\cos\vartheta)=4\pi\sum_{m=-l}^{l}Y_{lm}(\theta,\phi)Y_{lm}^*(\theta',\phi')\,, \quad (12)$$

where θ, ϕ are the polar angles of $\mathbf{q}$, and θ', ϕ' those of $\mathbf{r}$, referred to some fixed axis. Equation (1) for $f_{nlm}(\mathbf{q})$ now reads

$$f_{nlm}(\mathbf{q})=4\pi\sum_{l'm'}i^{l'}Y_{l'm'}(\theta,\phi)\int d\mathbf{r}R_{nl}(r)j_{l'}(qr) \times Y_{lm}Y_{l'm'}^*. \quad (13)$$

The orthogonality relation for spherical harmonics, together with the addition theorem (12), now leads directly from (13) to

$$\sum_{m=-l}^{l}f_{nlm}(\mathbf{q})f_{nlm}^*(\mathbf{q}')=4\pi(2l+1)I_{nl}(q) \times I_{nl}(q')P_l(\cos\phi)\,, \quad (14)$$

where ϕ is the angle between the vectors $\mathbf{q}$ and $\mathbf{q}'$, and $I(q)$ is the integral

$$I_{nl}(q)=\int_0^\infty r^2dr\,j_l(qr)R_{nl}(r) =\frac{n}{4\lambda^{3/2}}\left\{\frac{(n-l-1)!}{(n+l)!}\right\}^{1/2}\frac{1}{(n+l)!}\int_0^\infty x^{l+2}e^{-x/2} \times j_l(zx/2)L_{n-l-1}^{2l+1}(x)dx. \quad (15)$$

z is defined by

$$z=nq/\lambda. \quad (16)$$

The integral in (15) may be expressed in terms of Gegenbauer polynomials as[9]

$$\int_0^\infty e^{-x/2}x^{l+2}j_l(zx/2)L_{n-l-1}^{2l+1}(x)=\frac{8(2\pi)^{1/2}n(n+l)!}{(z^2+1)^2} \times\left\{\frac{2z}{z^2+1}\right\}^lT_{n-l-1}^{l+\frac{1}{2}}\left(\frac{z^2-1}{z^2+1}\right), \quad (17)$$

where $T_i^\beta(y)$ is the Gegenbauer polynomial, defined by

[3] D. R. Bates and A. Dalgarno, Proc. Phys. Soc. (London) **A66**, 972 (1953).
[4] J. R. Oppenheimer, Phys. Rev. **31**, 349 (1928).
[5] S. T. Butler, R. M. May, and I. D. S. Johnston, Phys. Letters (to be published).
[6] S. T. Butler and I. D. S. Johnston, Nucl. Fusion (to be published).
[7] R. M. May, Nucl. Fusion (to be published).
[8] J. R. Hiskes and M. H. Mittleman, U. S. Atomic Energy Commission Report UCRL-9969 1962, p. 128 (unpublished).

[9] This expression may be obtained straightforwardly by use of the generating functions (10) and (18) for the Laguerre and Gegenbauer polynomials together with the integral.

$$\int_0^\infty r^{l+1}j_l(ar)\exp(-br)dr=2^ll!a^l(a^2+b^2)^{-l-1}.$$

See also H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957), p. 39.

the generating function

$$\frac{2^\beta}{(1+t^2-2ty)^{\beta+\frac{1}{2}}}=\frac{\pi^{1/2}}{\Gamma(\beta+\frac{1}{2})}\sum_{i=0}^{\infty} t^i T_i^\beta(y). \tag{18}$$

$T_i^0(y)$ are just the Legendre polynomials $P_i(y)$, and $T_i^{1/2}(y)$ are Tschebyscheff polynomials.

Introducing the notation

$$\cos\theta\equiv\frac{z^2-1}{z^2+1};\quad \cos\theta'\equiv\frac{(z')^2-1}{(z')^2+1}, \tag{19}$$

and consequently

$$\sin\theta=\frac{2z}{z^2+1};\quad \sin\theta'=\frac{2z'}{(z')^2+1}, \tag{20}$$

we may use (15) and (17) in Eq. (14) to write

$$\sum_{m=-l}^{l} f_{nlm}(\mathbf{q})f_{nlm}^*(\mathbf{q}')=\frac{2^5\pi^2n^4(2l+1)}{\lambda^3(z^2+1)^2(z'^2+1)^2}\times\frac{(n-l-1)!}{(n+l)!}(\sin\theta\sin\theta')^l \times T_{n-l-1}^{l+\frac{1}{2}}(\cos\theta)T_{n-l-1}^{l+\frac{1}{2}}(\cos\theta')T_l^0(\cos\phi). \tag{21}$$

Putting $\mathbf{q}=\mathbf{q}'$ implies $\theta=\theta'$ and $\phi=0$, so that we have as a special case

$$\sum_{m=-l}^{l}|f_{nlm}(\mathbf{q})|^2=\frac{2^5\pi^2n^4(2l+1)}{\lambda^3(z^2+1)^4}\frac{(n-l-1)}{(n+l)!}\left\{\frac{2z}{z^2+1}\right\}^{2l}\times\left\{T_{n-l-1}^{l+\frac{1}{2}}\left(\frac{z^2-1}{z^2+1}\right)\right\}^2, \tag{22}$$

which could be useful in some physical contexts. We proceed to the much simpler expressions obtained on summing over l.

An addition theorem for Gegenbauer polynomials states that[10]

$$\sum_{l=0}^{n-1}(2l+1)[(n-l-1)!/(n+l)!](\sin\theta\sin\theta')^l \times T_{n-l-1}^{l+\frac{1}{2}}(\cos\theta)T_{n-l-1}^{l+\frac{1}{2}}(\cos\theta')T_l^0(\cos\phi) =(2/\pi)^{1/2}T_{n-1}^{1/2}(\cos\theta\cos\theta'+\sin\theta\sin\theta'\cos\phi). \tag{23}$$

Using this in (21) leads to the result

$$\sum_{l=0}^{n-1}\sum_{m=-l}^{l} f_{nlm}(\mathbf{q})f_{nlm}^*(\mathbf{q}')=\frac{2^6\pi^2n^4}{\lambda^3(2\pi)^{1/2}}\times\frac{1}{(z^2+1)^2((z')^2+1)^2}T_{n-1}^{1/2}(\cos\theta\cos\theta' +\sin\theta\sin\theta'\cos\phi), \tag{24}$$

[10] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), Vol. I, p. 784.

where θ and θ' are given in terms of q and q' by the definitions (16) and (19), and ϕ is the angle between the directions of $\mathbf{q}$ and $\mathbf{q}'$.

Finally, in the special case when $\mathbf{q}=\mathbf{q}'$ we have $\theta=\theta'$ and $\phi=0$ which, together with the fact that

$$T_{n-1}^{1/2}(1)=(2/\pi)^{1/2}n, \tag{25}$$

leads to Eq. (2), namely

$$\sum_{l=0}^{n-1}\sum_{m=-l}^{l}|f_{nlm}(\mathbf{q})|^2=2^6\pi n^5/\lambda^3(z^2+1)^4. \tag{26}$$

The above Eq. (24), which is relevant to certain impact parameter calculations, seems to be rather complicated in the general case ($\cos\theta\cos\theta'+\sin\theta\sin\theta'\times\cos\phi$ is not a simple function of $\mathbf{q}$ and $\mathbf{q}'$); however, for small n the equation is simple, and for large n asymptotic forms may be employed.

3. THEOREMS ON $g_{nlm}(q)$

For the physical applications we have in mind, we need not only $f_{nlm}(\mathbf{q})$ but also the matrix elements $g_{nlm}(\mathbf{q})$ defined by Eq. (4). A relation between $f_{nlm}(\mathbf{q})$ and $g_{nlm}(\mathbf{q})$ involving only q and n may be obtained directly from the Schrödinger equation for the H atom. In three-dimensional form, the wave equation for an eigenvector with principal quantum n reads

$$-\nabla^2\phi_{nlm}(\mathbf{r})-(2\lambda/r)\phi_{nlm}(\mathbf{r})=-(\lambda^2/n^2)\phi_{nlm}(\mathbf{r}). \tag{27}$$

Taking the Fourier transform of this equation with respect to $\mathbf{q}$, and using the fact that $\phi_{nlm}(\mathbf{r})$ vanishes at infinite distances, we get

$$(q^2+\lambda^2n^{-2})f_{nlm}(\mathbf{q})=2\lambda g_{nlm}(\mathbf{q}) \tag{28}$$

with $f(\mathbf{q})$ and $g(\mathbf{q})$ defined by (1) and (4).

Thus each of the addition theorems (21), (22), (24), and (26) may be converted to the corresponding equation involving the functions $g(\mathbf{q})$, since the conversion factor [namely $(z^2+1)/2n$] is dependent only on the principal quantum number n and the modulus of the vector $\mathbf{q}$.

A family of other matrix elements may be related to $f(\mathbf{q})$ by multiplying the Schrödinger equation by powers of r before performing the Fourier transform: for example multiplication by r^{-1} leads to

$$\int\frac{d\mathbf{r}}{r^2}\phi_{nlm}(\mathbf{r})\left\{1-\frac{i\mathbf{q}\cdot\mathbf{r}}{\lambda r}\right\}\exp(i\mathbf{q}\cdot\mathbf{r}) =\frac{1}{4\lambda^2}(q^2+\lambda^2n^{-2})^2f_{nlm}(\mathbf{q}). \tag{29}$$

Addition theorems corresponding to (24) and (26) are then obtained for these related matrix elements; however, since we have no application in mind for these functions we shall not consider them further.

4. SOME APPLICATIONS

In this section we consider two applications of the general theorems (2) and (5) which have been proved in Secs. 2 and 3.

Firstly we consider charge-exchange reactions of the type $H^+ + H(n_1l_1m_1) \rightarrow H(n_2l_2m_2) + H^+$. For such reactions proceeding from the initial H-atom state $n_1l_1m_1$ to the final state $n_2l_2m_2$ we can write the cross section in Born approximation as[11]

$$\sigma(n_1l_1m_1|n_2l_2m_2) = (2\pi p)^{-2}\int\int dg_x dg_y |f_1(\mathbf{q})|^2 \times |g_2(\mathbf{Q})|^2, \quad (30)$$

where the proton mass has been taken as infinite, and p is the (dimensionless) speed of the incident proton relative to the target H atom:

$$p \equiv \hbar v/e^2. \quad (31)$$

The proton has been taken incident along the z axis, and the vectors $\mathbf{q}$ and $\mathbf{Q}$ consequently have components

$$\mathbf{q} = \left(q_x, q_y, \left[p^2 - \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\right]\frac{\lambda}{2p}\right), \quad (32)$$

$$\mathbf{Q} = \left(q_x, q_y, \left[p^2 + \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\right]\frac{\lambda}{2p}\right). \quad (33)$$

We also note the identity[12]

$$q^2 + \lambda^2/n_1^2 = Q^2 + \lambda^2/n_2^2. \quad (34)$$

The matrix elements $f(\mathbf{q})$ and $g(\mathbf{Q})$ in (30) are, of course, just those defined by Eqs. (1) and (4) above.

If we now sum over the final-state quantum numbers l_2 and m_2 for a given n_2, and average over the initial quantum numbers l_1 and m_1 for a given n_1, we can immediately make use of the theorems (2) and (5) to write

$$\sigma(\langle n_1\rangle|n_2) = \frac{2^8\lambda^8}{p^2 n_1^5 n_2^3}\int\int \frac{dq_x dq_y}{(q_x^2 + q_y^2 + \lambda^2\beta)^6}. \quad (35)$$

This total cross section is defined by Eq. (7), and $\beta(p,n_1,n_2)$ is defined as

$$\beta(p,n_1,n_2) \equiv \frac{1}{4p^2}\left\{p^4 + 2p^2\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right) + \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)^2\right\}. \quad (36)$$

The integral in (35) is trivial, and we thus get for the cross section in Born approximation the fully exact result

$$\sigma(\langle n_1\rangle|n_2) = \pi a_0^2 \frac{2^8}{5n_1^5 n_2^3}\frac{1}{p^2\beta^5}. \quad (37)$$

For the special case where the initial H atom is in the ground state ($n_1=1$, $l_1=0$, $m_1=0$), Eq. (37) yields

$$\sigma(1|n_2) = \pi a_0^2 \frac{2^8}{5n_2^3}\frac{1}{p^2\{\alpha(p,n_2)\}^5}, \quad (38)$$

with $\alpha(p,n_2)$ given by the appropriate specialization of (36):

$$\alpha(p,n_2) = \frac{1}{4p^2}\left\{p^4 + 2p^2\left(1 + \frac{1}{n_2^2}\right) + \left(1 - \frac{1}{n_2^2}\right)^2\right\} \quad (39)$$

$$\approx \{(p^2+1)/2p\}^2 \quad \text{for} \quad n_2 \gg 1. \quad (40)$$

For a second application of our theorems, we consider the ionization of H atoms both by the photoelectric process and by collisions with ions and atoms.

Suppose we have a H atom, with initial quantum numbers n, l and m, which is to be ionized by photons, with energy $\hbar\omega$, incident along the z axis and polarized with their electric vector along the x axis. We assume that the final state of the electron can be written to sufficient accuracy by the plane wave $\phi(\mathbf{r}) = L^{-3/2} \times \exp(i\mathbf{k}\cdot\mathbf{r})$ (this corresponds to Born approximation). Then for the differential cross section we can write the standard result[13]

$$\sigma(nlm|\mathbf{k})d\Omega = \frac{e^2 k k_x^2}{2\pi m c \omega}\left|\int d\mathbf{r}\phi_{nlm}(\mathbf{r})e^{i\mathbf{q}\cdot\mathbf{r}}\right|^2 d\Omega, \quad (41)$$

where the modulus of the final-state wave vector $\mathbf{k}$ is given by

$$k^2 = 2m\omega/\hbar - \lambda^2/n^2. \quad (42)$$

The vector $\mathbf{q}$ in the matrix element is given by the analog of Eq. (32) for this problem:

$$\mathbf{q} = \boldsymbol{\kappa} - \mathbf{k}. \quad (43)$$

$\boldsymbol{\kappa}$ is the wave vector of the photon, having modulus ω/c and directed along the z axis.

If we wish to find the average cross section for photoelectric ionization of H atoms with a given initial principal quantum number n, we average over l and m.

[11] See Refs. 3 or 4. We have written Eq. (30) in the form in which it appears from an alternative impact parameter calculation given in Ref. 6. Such an impact parameter derivation was first given by J. A. Gaunt [Proc. Cambridge Phil. Soc. 23, 732 (1927)] in a different context. The identity between such impact parameter calculations and the usual Born approximation has been rigorously established by J. W. Frame [Proc. Cambridge Phil. Soc. 27, 511 (1931)]. For an excellent summary see T-Y. Wu and T. Ohmura, *Quantum Theory of Scattering* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962), Sec. M.

[12] A general symmetry theorem for rearrangement collisions [see for example M. Gell-Mann and M. L. Goldberger, Phys. Rev. 91, 398 (1953)] asserts that in the expression (30) for the cross section it does not matter whether we take $|f_1(\mathbf{q})g_2(\mathbf{Q})|$ or, instead, $|g_1(\mathbf{q})f_2(\mathbf{Q})|$. From the relation (28) between $f(\mathbf{q})$ and $g(\mathbf{q})$ together with (34) we can understand the bookkeeping in this symmetry theorem.

[13] See, for example, L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), p. 273.

Noting that the matrix element in (41) is of the form (1), we may use theorem (2) to write the average differential cross section

$$\sigma(\langle n\rangle|\mathbf{k})d\Omega=\frac{32e^2\lambda^5kk_x^2}{mc\omega n^5}\frac{d\Omega}{\{(\boldsymbol{\kappa}-\mathbf{k})^2+\lambda^2n^{-2}\}^4}. \quad (44)$$

The total cross section is found by integrating over angles for $\mathbf{k}$ and is

$$\sigma(\langle n\rangle|k)=\frac{128\pi e^2\lambda^5}{3mc\omega n^5}\frac{k^3}{\{(\lambda^2n^{-2}+k^2+\kappa^2)^2-4k^2\kappa^2\}^2}, \quad (45)$$

with k^2 given in terms of ω and n by Eq. (42). The Born approximation will be valid so long as the incoming photon frequency is large compared to the initial characteıistic frequency of the atomic electron: Using (42) this criterion can be expressed in terms of the speed of the outgoing free electron ($mv\equiv\hbar k$) as the requirement

$$\hbar v/e^2>1/n. \quad (46)$$

In the limit where the initial atom is in a highly excited state [and in general so long as (46) is strongly fulfilled], we may simplify Eq. (45) to read

$$\sigma(\langle n\rangle|k)=\pi a_0^2\frac{256\alpha}{3n^5}\left(\frac{\alpha\lambda}{2\kappa}\right)^{7/2}\frac{1}{(1-\alpha\kappa/2\lambda)^4}, \quad (47)$$

where α is the fine-structure constant, $\alpha=e^2/\hbar c$. Equations (44), (45), and (47) are well-known results in the most interesting case when the H atom is initially in its ground state, $n=1$.

We next consider the case where the H atom is ionized by collisions with massive particles (massive in the sense that their mass may be taken to be infinite compared to the electron mass).

By means of an impact parameter calculation similar to that performed in Ref. 6, we get an expression[14] for the cross section for ionization of a H atom (initially in the state n, l, m) by bombardment with massive particles (incident parallel to the z axis and with speed v relative to the target atom):

$$\sigma(nlm|\mathbf{k})=\frac{1}{(2\pi\hbar v)^2L^3}\int d\mathbf{q}|U(\mathbf{q})|^2\times\frac{1}{2\pi}\int_{-\infty}^{+\infty}dz\exp\{iz(\omega_{nk}/v+q_z)\}, \quad (48)$$

$$U(\mathbf{q})=\int d\mathbf{R}V(\mathbf{R})e^{i\mathbf{q}\cdot\mathbf{R}}\int d\mathbf{r}\phi_{nlm}(\mathbf{r})e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}}. \quad (49)$$

Again the final state is represented by plane waves with wave vector $\mathbf{k}$ (i.e., Born approximation): $\hbar\omega_{nk}$ is the electron energy difference,

$$\omega_{nk}/v=-(\lambda^2n^{-2}+k^2)/2\lambda p, \quad (50)$$

with p defined by (31). $V(\mathbf{r})$ is the interaction potential between an electron and the passing particle when they are separated by a distance r, and $V(\mathbf{q})$ is the Fourier transform of this potential: for example if the ionizing particle is a proton,

$$V(\mathbf{r})=e^2/r;\quad V(\mathbf{q})=4\pi e^2/q^2 \quad (51)$$

and if it is a H atom in the ground state,

$$V(\mathbf{r})=\frac{e^2}{r}-e^2\int|\phi_{100}(\mathbf{R})|^2\frac{d\mathbf{R}}{|\mathbf{r}-\mathbf{R}|}, \quad (52)$$

$$V(\mathbf{q})=4\pi e^2(8\lambda^2+q^2)/(4\lambda^2+q^2)^2.$$

We see that (48) contains a matrix element of just the kind defined by (1). If we average over all l and m for a target H atom in the given excited state n, we may use our theorem (2) to get

$$\sigma(\langle n\rangle|\mathbf{k})=\frac{2^4\lambda^5}{\pi L^3(\hbar v)^2n^5}\int d\mathbf{q}\delta(q_z+\omega_{nk}/v)|V(\mathbf{q})|^2\times\{\lambda^2n^{-2}+(\mathbf{q}-\mathbf{k})^2\}^{-4}. \quad (53)$$

If we now compute the total cross section for ionizing collisions, by integrating over all final states $\mathbf{k}$ [using the density function $\rho(\mathbf{k})d\mathbf{k}=(2\pi)^{-3}L^3d\mathbf{k}$], we get an expression which in general will be reasonably tractable:

$$\sigma(\langle n\rangle|\text{free})=\frac{2\lambda^5}{\pi^4(\hbar v)^2n^5}\int d\mathbf{k}\int d\mathbf{q}\delta(q_z+\omega_{nk}/v)\times|V(\mathbf{q})|^2\{\lambda^2n^{-2}+(\mathbf{q}-\mathbf{k})^2\}^{-4}. \quad (54)$$

The special case of target H atoms in the ground state, $n=1$, is of course well known for all physically interesting interactions $V(\mathbf{r})$.

Our expression (54) also leads to a particularly simple expression in the limit $n\gg1$ provided that $V(\mathbf{q})$ is regular and square-integrable. [Our exemplifying potential (51) is *not* regular at the origin, but (52) is both regular and square-integrable.] In this limit we notice that because of the last factor in the integrand in (54) we must have $|\mathbf{k}|=|\mathbf{q}|$ up to order $1/n^2$, so that (54) can be written as

$$\sigma(\langle n\rangle|\text{free})=\frac{1}{(2\pi\hbar v)^2}\int d\mathbf{q}|V(\mathbf{q})|^2\delta(q_z-(q^2/2\lambda p)). \quad (55)$$

We have neglected all terms of relative order $1/n^2$, which will be permissible in the limit $n\gg1$ provided $V(\mathbf{q})$ satisfies the conditions required above. Equation (55) can be written in simpler form as

$$\sigma(\langle n\rangle|\text{free})=\frac{1}{2\pi(\hbar v)^2}\int_0^{2\lambda p}qdq\{V(q)\}^2. \quad (56)$$

[14] This is a simple generalization of the expression given by Wu and Ohmura [Ref. 11, p. 225, Eqs. (M56) and (M57)].

We have given no illustration of the use of the more complicated addition theorem (24) for $|f(\mathbf{q})f(\mathbf{q}')|$. We plan to use this result in an impact parameter calculation to examine the validity of Born approximation for the charge-exchange cross section $\sigma(\langle n_1\rangle|n_2)$ for various values of n_1 and n_2.

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Measurements of Electron Capture in Close H^+-on-He and He^+-on-H Collisions*

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Differential measurements of electron capture probability P_0 are made for close encounters in the reaction $H^+ + He \rightarrow H + He^+$. The energy range of the incident proton is 1.6 to 180.0 keV and the scattering angle is varied from $\frac{1}{2}$ to 4°. The impact parameters associated with these collisions extend from 0.015 to about 0.50 Å. There is little angular dependence to the data. When P_0 is plotted versus energy, a damped resonant structure is seen with peaks at 36, 7, and 2.6 keV with amplitudes of 0.52, 0.16, and 0.05, respectively. The phenomena are discussed in terms of the energy-level diagram for HeH^+ and with reference to the existing theories for charge transfer in the nonresonant case. Measurements of the inverse reaction, He^+ ions incident on atomic hydrogen targets, are also presented and discussed.

1. INTRODUCTION

RESONANT electron capture in violent (or close) single encounters in symmetrical or "resonant" ion-atom systems has been studied in several experiments[1] and the pertinent theory[2–4] explains many of the observed features. However, a somewhat similar phenomenon found in the unsymmetrical or "nonresonant" reaction

$$H^+ + He \rightarrow H + He^+, \quad (\Delta E = +11 \text{ eV}), \quad (1)$$

is not well understood.

Differential scattering measurements of the above reaction were first made by Ziemba *et al.*[5] These covered the energy range of 2 to 180 keV. The incident protons were driven through the electronic structure of helium atoms at impact parameters sufficiently small to deflect the fast particles through an angle of 5°. The probability P_0 of electron capture by a proton in such a single collision was measured. When P_0 was plotted versus incident energy T, a damped resonant structure was seen.

The purpose of the present study is to repeat these measurements of H^+ on He collision with considerably improved accuracy, and further, to study the angular dependence as well as the energy dependence of the quantity P_0, thus varying both the impact parameter and the velocity of the collision.

In addition, similar measurements of the inverse reaction,

$$He^+ + H \rightarrow He + H^+, \quad (\Delta E = -11 \text{ eV}), \quad (2)$$

are also studied here, making use of the atomic hydrogen target chamber previously developed for the H^+ on H studies.[1]

There is, at present, no published theory in a form readily applicable to the reactions (1) and (2) under study here. The general theory of charge transfer in nonresonant collisions is that of Bates, Massey, and Stewart[6] as improved by Takayanagi,[7] and Bates and McCarroll.[8] Further contributions by Bates and Lynn,[9]

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