Effect of Virtual Excitation of the 2s State on the Elastic Scattering of Electrons by Atomic Hydrogen*

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The elastic scattering of electrons by hydrogen atoms, for electron energies below the first threshold of excitation of the atom (10.2 ev), is investigated numerically making full allowance for exchange and for the virtual excitation of the 2s state. Singlet and triplet phases for the s, p, and d partial waves have been obtained. While the calculation is essentially preliminary to a more extensive eigenfunction expansion calculation for this problem, which would allow for nonspherical distortion of the atom, the results do show that significant changes from the first exchange approximation may be expected as one includes more states in the expansion. In particular, just below the n=2 excitation threshold the singlet s phase and the triplet p phases begin to increase sharply, and what may be a Wigner cusp shows in the total cross section. Predicted angular distributions are compared with the recent measurements of Gilbody, Stebbings, and Fite. The phase shifts are compared with those of the exchange approximation, and also with those of Geltman, who performed a variational calculation allowing for the virtual excitation of the 2s and 3s states.

INTRODUCTION

IN a recent paper Smith and Burke[1] presented a few preliminary results for the singlet and triplet s phases for the problem of electron collisions with hydrogen atoms, in the so-called strong-coupling approximation with allowance for exchange, for energies below the threshold of excitation of the n=2 level of hydrogen. It is recalled that in this approximation, the eigenfunction expansion of the wave function includes only the 1s and 2s states of atomic hydrogen, with exchange being allowed for by symmetrizing and antisymmetrizing the trial function for the singlet and triplet cases, respectively. In this paper the results of numerical calculations in this approximation over the entire energy range below the n=2 threshold are presented for the partial waves l=0, 1, and 2.

It is realized that this approximation is but a step towards a more complete eigenfunction expansion calculation, including further bound states of the hydrogen atom (in particular the p states) to allow for the nonspherical distortion or polarization of the atom.[2] The 2p state alone contributes some $\frac{2}{3}$ of the polarizability of hydrogen (e.g., Castillejo et al.[3]).

In Sec. I the numerical methods of solution of the coupled integro-differential equations are discussed. The results are presented in Sec. II, where they are compared with those of the exchange approximation[4] and with those of Geltman,[5] who used a variational method to examine the effect of virtual excitation of the 2s and 3s states, making full allowance for exchange. Predicted angular distributions are compared with those measured by Gilbody et al.,[6] and for two energies with those predicted by the exchange approximation.

I. MATHEMATICAL METHOD

Explicitly, the assumed forms of trial functions in this approximation are

$$\Psi^{\pm}(\mathbf{r}_1,\mathbf{r}_2)=\psi_{1s}(\mathbf{r}_1)F_0(\mathbf{r}_2)+\psi_{2s}(\mathbf{r}_1)F_1(\mathbf{r}_2)\pm(\mathbf{r}_1\leftrightarrow\mathbf{r}_2),\quad(1)$$

for the singlet and triplet cases respectively. Expanding

[1] Kenneth Smith and P. G. Burke, Phys. Rev. 123, 174 (1961).
[2] P. G. Burke, V. M. Burke, and H. M. Schey, *Second International Conference on the Physics of Electronic and Atomic Collision, University of Colorado, Boulder, June 12–15, 1961* (W. A. Benjamin Inc., New York, 1961), paper I 2.
[3] L. Castillejo, I. C. Percival, and M. J. Seaton, Proc. Roy. Soc. (London) A254, 259 (1960).

[4] A set of exchange approximation phases have been presented by T. L. John, Proc. Phys. Soc. (London) 76, 532 (1960). The results quoted here, however, have been computed for the purposes of this paper by two of the authors (R.P.M. and P.A.F.). These agree with the results of John for energies for which comparison is directly possible. The l=1 and 2, and where possible, the l=0 exchange phases were computed by iteration on the integral equation formulation for the exchange approximation. Where this method diverged for the l=0 case (see text), solutions were obtained by the method of Percival, described by Marriott in reference 8. These authors (R.P.M. and P.A.F.) acknowledge that Geltman was correct in his suggestion, in reference 5, that their published exchange-approximation d phases [Can. J. Phys. 38, 317 (1960)] were too small in absolute value. The errors arose from an inadequate application of a numerical method, different from that used in this paper, to solve the integral equations. While the former approximation gave adequate results for the s phases and the larger p phases (>0.1 in absolute value, say), it failed, in the light of later work, to give good results for small phases.
[5] Sydney Geltman, Phys. Rev. 119, 1283 (1960).
[6] H. B. Gilbody, R. F. Stebbings, and Wade L. Fite, Phys. Rev. 121, 794 (1961).

F_0 and F_1 as follows:

$$F_0^{\pm}(\mathbf{r}) = \frac{1}{r} \sum_{l=0}^{\infty} f_l^{\pm}(r) P_l(\cos\vartheta), \qquad (2)$$

and

$$F_1^{\pm}(\mathbf{r}) = \frac{1}{r} \sum_{l=0}^{\infty} g_l^{\pm}(r) P_l(\cos\vartheta), \qquad (3)$$

one obtains, through the Kohn variational principle,[7] coupled integro-differential equations for the $f_l^{\pm}(r)$ and $g_l^{\pm}(r)$:

$$\left[\frac{d^2}{dr_1^2} + k^2 - \frac{l(l+1)}{r_1^2}\right] f_l^{\pm}(r_1)$$

$$= V_{00}(r_1) f_l^{\pm}(r_1) \pm \int_0^{\infty} dr_2\, K_{00}(r_1,r_2) f_l^{\pm}(r_2)$$

$$+ V_{01}(r_1) g_l^{\pm}(r_1) \pm \int_0^{\infty} dr_2\, K_{01}(r_1,r_2) g_l^{\pm}(r_2)$$

$$= G_l^{\pm}(r_1), \qquad (4)$$

$$\left[\frac{d^2}{dr_1^2} + k^2 - \frac{3}{4} - \frac{l(l+1)}{r_1^2}\right] g_l^{\pm}(r_1)$$

$$= V_{11}(r_1) g_l^{\pm}(r_1) \pm \int_0^{\infty} dr_2\, K_{11}(r_1,r_2) g_l^{\pm}(r_2)$$

$$+ V_{10}(r_1) f_l^{\pm}(r_1) \pm \int_0^{\infty} dr_2\, K_{10}(r_1,r_2) f_l^{\pm}(r_2)$$

$$= H_l^{\pm}(r_1). \qquad (5)$$

These equations are of the same form as those used by Marriott[8] and by Smith[9] in discussing excitation of the $2s$ level of hydrogen by electron impact. The explicit form of the potentials V and the kernels K are given by Erskine and Massey.[10] k^2 is the kinetic energy of the electron in units of 13.6 ev. The unit of length is a_0, the Bohr radius. In the present paper we are interested in the case $k^2 < \frac{3}{4}$, i.e., below the $n=2$ threshold of excitation. The boundary conditions on $f_l^{\pm}(r)$ and $g_l^{\pm}(r)$ are thus

$$f_l^{\pm}(r) \underset{r\to\infty}{\sim} \sin(kr - l\pi/2) + \tan\eta_l^{\pm} \cos(kr - l\pi/2),$$

$$g_l^{\pm}(r) \underset{r\to\infty}{\sim} A_l \exp(-\gamma_l r), \quad (\gamma_l^2 = \tfrac{3}{4} - k^2), \qquad (6)$$

with $f_l^{\pm}(0) = 0$, and $g_l^{\pm}(0) = 0$.

The damped exponential behavior of $g_l^{\pm}(r)$ follows from the energetic impossibility of real excitation of the

2s state of hydrogen. For exact solutions of Eqs. (4) and (5), the Kohn corrections to the approximate $\tan\eta_l^{\pm}$ are zero, and hence the values obtained are correct to second order in the difference between the exact total wave functions and the trial functions. The total scattering cross section (in units of πa_0^2) for an unpolarized electron beam is given by

$$\sigma = \frac{4}{k^9} \sum_{l=0}^{\infty} (2l+1)[\tfrac{1}{4} \sin^2\eta_l^{+} + \tfrac{3}{4} \sin^2\eta_l^{-}].$$

The angular distribution of the scattered electrons may also be expressed in terms of the phase shifts $\eta_l^{\pm}$.

Smith and Burke[1] have described an iterative numerical method of solution of these equations. It is recalled that this method involves integrating out from the origin to some r_0, and integrating in from the asymptotic region to r_0, and the solutions obtained by matching sums of linearly independent solutions. This method has been used by one of the authors (K.S.) for the $l=0$ phase shifts reported here, using an IBM-704. These results check with those obtained for this approximation by the IBM-709 code of reference 2.[11] A few $l=1$ phase shifts have been obtained by this method,[1] and these agree, at least away from the $n=2$ threshold, to 3 or 4 decimal places with the results obtained by the method described in succeeding paragraphs.

An alternative method, using an IBM-650, has been used by two of the authors (R.P.M. and P.A.F.), which is based on an iteration scheme for the integral equation formulation of the equations and boundary conditions. The method may be of considerable utility in more complicated problems as it generally converges very fast for $l>0$. Results have been obtained, and are presented here, for the $l=1$ and $l=2$ phases by this method; however, for $l=0$ the method diverges for $k \lesssim 0.3$ in the symmetric case and for $k \gtrsim 0.8$ in the antisymmetric case.

The integral equations equivalent to the integro-differential Eqs. (4) and (5) plus the boundary conditions (6) may be written as follows:

$$f_l^{\pm}(r_1) = u_l(kr_1) - \int_0^{\infty} dr_2\, \mathcal{L}_l(r_1,r_2) G_l^{\pm}(r_2), \qquad (8)$$

$$g_l^{\pm}(r_1) = - \int_0^{\infty} dr_2\, \mathcal{L}_l^1(r_1,r_2) H_l^{\pm}(r_2), \qquad (9)$$

where the Green's functions $\mathcal{L}_l$ and $\mathcal{L}_l^1$ are given by

$$\mathcal{L}_l(r_1,r_2) = u_l(kr_<) v_l(kr_>)/k, \qquad (10)$$

and

$$\mathcal{L}_l^1(r_1,r_2) = p_l(\gamma_1 r_<) q_l(\gamma_1 r_>)/\gamma_1, \qquad (11)$$

with $r_<$ the lesser of r_1 and r_2, and $r_>$ the greater. The functions $u_l(x)$, $v_l(x)$, $p_l(x)$ and $q_l(x)$ are given by the

[7] W. Kohn, Phys. Rev. **74**, 1763 (1948); B. M. Bransden, A. Dalgarno, T. L. John, and M. J. Seaton, Proc. Phys. Soc. (London) **71**, 877 (1958).
[8] R. Marriott, Proc. Phys. Soc. (London) **72**, 121 (1958).
[9] Kenneth Smith, Phys. Rev. **120**, 845 (1960).
[10] G. A. Erskine and H. S. W. Massey, Proc. Roy. Soc. (London) **A212**, 521 (1952).
[11] P. G. Burke (private communication).

relations[12]

$$u_l(x) = (\pi x/2)^{\frac{1}{2}}J_{l+\frac{1}{2}}(x),$$

$$v_l(x) = (-1)^l(\pi x/2)^{\frac{1}{2}}J_{-(l+\frac{1}{2})}(x), \quad (12)$$

$$p_l(x) = (\pi x/2)^{\frac{1}{2}}I_{l+\frac{1}{2}}(x), \quad q_l(x) = (2x/\pi)^{\frac{1}{2}}K_{l+\frac{1}{2}}(x). \quad (13)$$

The phase shifts are given by the integrals

$$\tan\eta_l^{\pm} = -\frac{1}{k}\int_0^{\infty} dr_2\, u_l(kr_2)G_l^{\pm}(r_2). \quad (14)$$

The iteration procedure starts by evaluating $H_l^{\pm}(r)$ with the $f_l^{\pm}(r)$ obtained from the exchange approximation and with $g_l^{\pm}(r) \equiv 0$. This value of $H_l^{\pm}(r)$ is substituted into Eq. (9) to yield a new $g_l^{\pm}(r)$, which in turn may be used to recalculate $H_l^{\pm}(r)$. This process is repeated, with $f_l^{\pm}(r)$ remaining fixed, until $g_l^{\pm}(r)$ converges. With this final value of $g_l^{\pm}(r)$ remaining fixed in the evaluation of $G_l^{\pm}(r)$ a similar iteration process is carried out with Eq. (8) to obtain a new $f_l^{\pm}(r)$. The entire procedure as outlined above is repeated (usually once or twice is sufficient) until Eqs. (8) and (9) are both simultaneously satisfied to the required accuracy. The integrals are necessarily cut off at some finite value of r (≈ 15); however it is possible to apply at each stage corrections in terms of the approximate asymptotic forms of the $f_l^{\pm}(r)$ and $g_l^{\pm}(r)$.

II. RESULTS

Tables I–III display s, p, and d phases calculated (a) in the exchange approximation, (b) including $2s$ virtual excitation, and (c) by Geltman.[5] Comparison of the present results with those of Geltman[5] suggest

TABLE I. $l=0$ phase shifts in radians. k^2 is the electron energy in units of 13.6 ev.

		(Triplet)			(Singlet)		
k	k^2	Exchange	Virtual $2s$	Geltman	Exchange	Virtual $2s$	Geltman
0.0[a]	0.0	2.35	2.33	2.350	8.10	7.5	8.220
0.01	0.0010		3.108			3.065	
0.05	0.0025		3.022			2.767	
0.075	0.0056		2.916			2.591	
0.1	0.01	2.908	2.901		2.396	2.404	2.389
0.2	0.04	2.679	2.6797	2.679	1.870	1.8776	1.834
0.3	0.09	2.461	2.4609		1.508	1.5190	1.489
0.4	0.16	2.257	2.2575	2.257	1.239	1.2569	1.201
0.45	0.2025		2.1619			1.1417	
0.5	0.25	2.070	2.0704		1.031	1.0406	
0.5286	0.2794	2.020	2.0193		0.9807	0.9965	
0.6	0.36	1.901		1.901	0.8690		0.8406
0.6474	0.4191	1.826	1.8245		0.8055	0.8284	
0.7	0.49	1.749	1.7529		0.7441		
0.7225	0.5220	1.720	1.7196		0.7205	0.7516	
0.8	0.64	1.614	1.616	1.616	0.6512	0.6977	0.5862
0.8314	0.6912	1.574	1.5775		0.6279	0.6877	
0.85	0.7225	1.552	1.5546		0.6153	0.6934	
0.8544	0.73	1.548	1.5493		0.6124	0.7004	
0.8602	0.74	1.541	1.5397		0.6087	0.732[b,c]	

[a] The $k=0$ entries are the scattering lengths in units of a_0^{-1}.
[b] The convergence of the iterative procedure was slow for this energy.
[c] A value of 0.834 was obtained for the singlet $l=0$ phase for $k^2=0.745$; this value should be regarded as provisional, as the convergence was indeed slow.

that for the p and d waves, the inclusion of the $3s$ state leads to no essential change in the phases. The zero-energy scattering lengths, $A_0^+=7.5$ and $A_0^-=2.33$, are still significantly greater than their corresponding upper limits of $A_0^+=6.23$ and $A_0^-=1.91$.[13] It is interesting to note the beginning of a sharp rise in the $l=0$ singlet and the $l=1$ triplet phases just below the threshold of excitation ($k^2=0.75$, $k=0.866$). Newton[14] has

TABLE II. $l=1$ phase shifts in radians. k^2 is the electron energy in units of 13.6 ev.

		(Triplet)			(Singlet)		
k	k^2	Exchange	Virtual $2s$	Geltman	Exchange	Virtual $2s$	Geltman
0.1	0.01	0.0022	0.0040	0.0048	−0.0012	−0.0003	+0.0008
0.15	0.0225	0.0072	0.0129		−0.0036	−0.0014	
0.2	0.04	0.0166	0.0281	0.0277	−0.0084	−0.0040	−0.0027
0.3	0.09	0.0511	0.0771		−0.0240	−0.0162	
0.4	0.16	0.1050	0.1422	0.1412	−0.0461	−0.0380	−0.0395
0.5	0.25	0.1694	0.2105		−0.0703	−0.0646	
0.5286	0.2794	0.1879	0.2289		−0.0769	−0.0722	
0.6	0.36	0.2318	0.2717	0.2774	−0.0920	−0.0894	−0.0901
0.6474	0.4191	0.2579	0.2968		−0.1003	−0.0989	
0.7	0.49	0.2833	0.3206		−0.1076	−0.1071	
0.7225	0.5220	0.2929	0.3304		−0.1101	−0.1097	
0.8	0.64	0.3204	0.3608	0.3624	−0.1154	−0.1140	−0.1158
0.8314	0.6912	0.3292	0.3783		−0.1160	−0.1133	
0.85	0.7225	0.3339	0.411		−0.1160	−0.1120	
0.8544	0.73	0.3349	0.438		−0.1160	−0.1115	
0.8602	0.74	0.3362	0.95[a]		−0.1159	−0.1109	

[a] See text; while the process was slow, the iteration on the integral equations converged in the sense that the $f_1^-(r)$ and $g_1^-(r)$ functions from the final stage agreed to five figures with the output of the previous stage. This is not to say that the result is accurate to five figures; taking account of truncation error the result is estimated to be good to possibly 2 figures. The method of Smith and Burke (reference 1), which was used to compute the values in Table I (virtual $2s$ approximation), converges extremely slowly for the triplet p wave near the $n=2$ excitation threshold, and gives for this phase 0.41 for $k^2=0.74$, and 0.47 for $k^2=0.745$. While the convergence criterion was satisfied, further iterations beyond this stage gave phases apparently diverging from the above values.

[12] N. W. McLachlan, *Bessel Functions for Engineers* (Oxford University Press, New York, 1955), 2nd ed.
[13] L. Rosenberg, L. Spruch, and T. O'Malley, Phys. Rev. 119, 165 (1960).
[14] Roger G. Newton, Ann. Phys. 4, 29 (1958).

TABLE III. $l=2$ phase shifts in radians. k^2 is the electron energy in units of 13.6 ev.

k	k^2	(Triplet)			(Singlet)		
		Exchange	Virtual 2s	Geltman	Exchange	Virtual 2s	Geltman
0.3	0.09	0.0008	0.0010		−0.0005	−0.0005	
0.4	0.16	0.0029	0.0034	0.0034	−0.0017	−0.0016	−0.0016
0.5	0.25	0.0070	0.0081		−0.0039	−0.0038	
0.5286	0.2794	0.0086	0.0099		−0.0047	−0.0046	
0.6	0.36	0.0135	0.0154	0.0148	−0.0070	−0.0069	−0.0070
0.6474	0.4191	0.0175	0.0197		−0.0087	−0.0086	
0.7	0.49	0.0223	0.0251		−0.0106	−0.0105	
0.7225	0.5220	0.0246	0.0276		−0.0114	−0.0113	
0.8	0.64	0.0327	0.0366	0.0365	−0.0139	−0.0138	−0.0140
0.8314	0.6912	0.0362	0.0406		−0.0148	−0.0147	
0.85	0.7225	0.0383	0.0430		−0.0152	−0.0151	
0.8544	0.73	0.0388	0.0436		−0.0154	−0.0153	
0.8602	0.74	0.0395	0.0444		−0.0155	−0.0154	

discussed, and given examples of, such behavior in phase shifts for energies approaching a threshold.

Tables IV and V show the differential cross sections given by the exchange and 2s virtual excitation approximations, for the energies 7.1 ev and 9.4 ev, the two largest energies for which Gilbody et al.[6] performed measurements. It is clear that the contribution of the d waves should not be ignored in discussion of the angular distribution. Figure 1 shows the present calculated angular distributions for the energies 3.8, 5.7, 7.1, and 9.4 ev, together with the measured points of Gilbody et al.[6] The gratifying agreement for the two highest energies should perhaps be regarded with some reservation in view of the great difficulty of the experiment and the stated experimental errors, and the incompleteness of the present physical approximation.

As pointed out by Temkin and Lamkin,[15] a measurement of the spin-flip cross section[16] will help to distinguish between sets of published phases. In Table VI are shown these cross sections together with the total elastic scattering cross sections for various energies as given by the exchange approximation and by the 2s virtual excitation approximation. Figure 2 shows the total elastic cross section as a function of energy: below the $n=2$ threshold the values are those from the 2s virtual excitation approximation, reported here; above the threshold the values are those obtained by Smith.[9]

Particularly noticeable is the occurrence at the $n=2$ excitation threshold of what may be a Wigner cusp in the cross section. These cusps, and other threshold behaviors, have also been discussed by Newton.[14] The sharp rise is attributable to the contributions of the singlet s wave and the triplet p wave, the behavior of whose phase shifts near threshold has been noted earlier. The numerical methods used in the present calculations either do not work satisfactorily or are very slowly convergent near the threshold for the partial waves just mentioned. For example, while a representative normal p-wave calculation took ~ 1 hr on an IBM 650, the triplet p-wave calculation at $k^2=0.74$ took ~ 10 hr before convergence was satisfactory, and even then it was found necessary at certain iteration stages to multiply $g_1^-(r)$ by a suitable constant to speed convergence.

TABLE IV. Differential cross section for energy 7.1 ev ($k^2 = 0.5220$) in units of πa_0^2 per steradian, as given by the exchange approximation and the virtual 2s approximation, with and without the d-wave contributions.

Scattering angle	Exchange		Virtual 2s	
	$s+p$	$s+p+d$	$s+p$	$s+p+d$
0°	0.941	1.025	1.082	1.191
15°	0.914	0.987	1.048	1.141
30°	0.842	0.884	0.955	1.010
45°	0.741	0.754	0.824	0.840
60°	0.637	0.634	0.684	0.683
75°	0.555	0.555	0.578	0.576
90°	0.514	0.527	0.518	0.532
105°	0.520	0.541	0.519	0.542
120°	0.570	0.579	0.574	0.584
135°	0.646	0.623	0.662	0.635
150°	0.725	0.660	0.756	0.679
165°	0.784	0.683	0.827	0.707
180°	0.806	0.691	0.854	0.716

[15] A. Temkin and J. C. Lamkin, Phys. Rev. 121, 788 (1961).
[16] $\sigma_f = (1/4k^2)\Sigma_{l=0}^{\infty}(2l+1)\sin^2(\eta_l^+ - \eta_l^-)$ in units of πa_0^2.

TABLE V. Differential cross section for energy 9.4 ev ($k^2 = 0.6912$) in units of πa_0^2 per steradian, as given by the exchange approximation and the virtual 2s approximation, with and without the d-wave contributions.

Scattering angle	Exchange		Virtual 2s	
	$s+p$	$s+p+d$	$s+p$	$s+p+d$
0°	0.904	1.034	1.072	1.236
15°	0.875	0.987	1.035	1.176
30°	0.795	0.863	0.930	1.016
45°	0.682	0.703	0.782	0.809
60°	0.560	0.553	0.623	0.614
75°	0.454	0.445	0.484	0.472
90°	0.385	0.390	0.392	0.397
105°	0.361	0.377	0.358	0.378
120°	0.380	0.388	0.379	0.390
135°	0.427	0.405	0.438	0.411
150°	0.483	0.419	0.509	0.430
165°	0.527	0.427	0.565	0.441
180°	0.544	0.430	0.586	0.445

TABLE VI. Partial and total elastic cross sections and spin-flip cross section (in units of πa_0^2).

Kinetic energy		Virtual 2s				Exchange	Virtual 2s	Exchange
(ev)	k^2	σ_0	σ_1	σ_2	σ	σ	σ_f	σ_f
0.00	0.00	72.5			72.5	82.2	6.68	8.27
0.14	0.01	62.3	0.01	0.000	62.3	62.1	5.68	6.00
0.54	0.04	37.6	0.18	0.000	37.8	37.8	3.24	3.28
1.2	0.09	24.3	0.60	0.000	24.9	24.5	1.89	1.89
2.2	0.16	16.9	1.16	0.001	18.0	17.5	1.26	1.23
3.4	0.25	12.2	1.62	0.004	13.8	13.3	0.957	0.913
3.8	0.2794	11.2	1.71	0.006	13.0	12.4	0.889	0.850
5.7	0.4191	8.00	1.91	0.015	9.92	9.42	0.688	0.655
7.1	0.5220	6.51	1.88	0.023	8.42	7.98	0.589	0.562
8.7	0.64	5.32	1.81	0.033	7.17	6.74	0.496	0.476
9.4	0.6912	4.92	1.83	0.037	6.79	6.28	0.466	0.444
9.8	0.7225	4.72	2.04	0.040	6.79	6.04	0.463	0.426
9.9	0.73	4.68	2.27	0.041	6.99	5.98	0.479	0.422
10.1	0.74	4.65[a]	8.1[a]	0.042	12.8[a]	5.90	0.95[a]	0.416

[a] See footnote b of Table I, and footnote a of Table II.

III. CONCLUDING REMARKS

The results reported here point up that interesting effects may occur at excitation thresholds in atomic collision problems. The computer effort should however perhaps be placed on more realistic physical approximations (e.g., that of reference 2), rather than on that used here.

While important and elegant calculations, by very different methods, of the s phases for this problem have been reported by Temkin[17] and Schwartz,[18] it is not inconceivable that the eigenfunction expansion approach is the most practical for orbital angular momenta greater than zero, and may also provide the most practical approach to problems involving more complicated atoms than hydrogen.
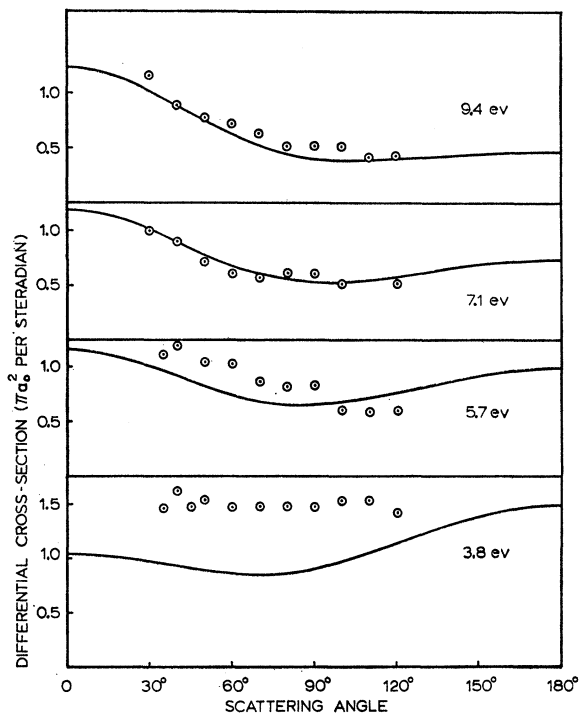

FIG. 1. The angular distribution of electrons scattered elastically by atomic hydrogen at various energies, as given by the virtual 2s approximation (solid line). The circled points represent the experimental results of Gilbody et al. (reference 6).
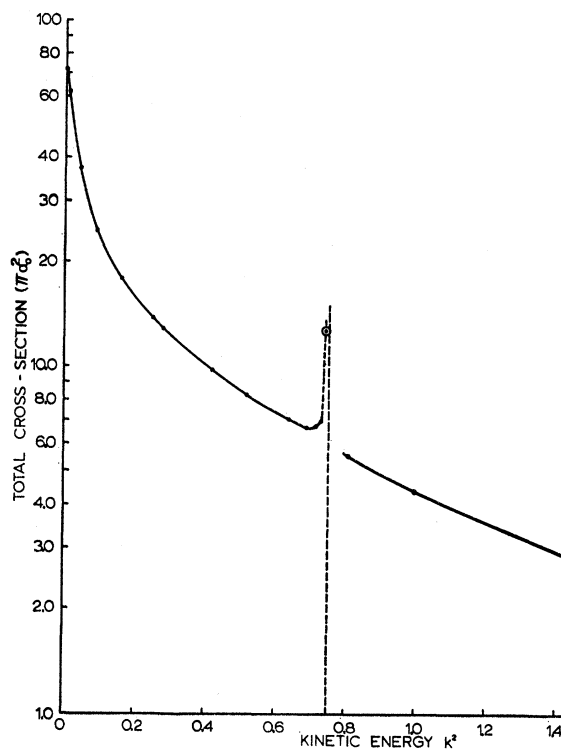

FIG. 2. The total cross section for the elastic scattering of electrons by atomic hydrogen. The $n=2$ excitation threshold is marked by the vertical dashed line. The kinetic energy is k^2 in units of 13.6 ev. The validity of the circled point (at $k^2=0.74$) has been discussed in the text and particularly in footnotes to Tables I and II.

[17] A. Temkin, Phys. Rev. Letters 4, 566 (1960), and Second International Conference on the Physics of Electronic and Atomic Collisions, University of Colorado, Boulder, June 12–15, 1961 (W. A. Benjamin Inc., New York, 1961), paper I 5.

[18] C. Schwartz, Second International Conference on the Physics of Electronic and Atomic Collisions, University of Colorado, Boulder, June 12–15, 1961 (W. A. Benjamin Inc., New York, 1961), paper I 1.

Transition Probability due to Random Perturbations

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The subject of transition probabilities induced by random perturbations is treated. The expression for average transition rates between two energy levels is derived for the general case when the frequency spectrum of the perturbation and the distribution of the energy levels have comparable widths. The general expression takes an especially simple form for the special cases where the frequency bandwidth of the perturbation Hamiltonian is either much larger or much smaller than that of the energy level distribution. The formulas are applied, by way of illustration, to a number of physical problems.

INTRODUCTION

THIS paper attempts to present, from a unified point of view, the effect of random perturbations on transitions between two energy levels. It is shown that the degree of randomness of a given perturbation is characterized by Ω_1/Ω_0, the ratio of the spectral bandwidth of the perturbation to the width of the energy level distribution. The theory has a strong bearing on the case of motional narrowing of resonance lines, which has been studied in detail by Bloembergen et al.[1] Some of the features of the motional narrowing theory are rederived as a special case.

THEORY

The starting point for first-order time-dependent perturbation theory is usually the equation[2]

$$a_k(t) = (i\hbar)^{-1} \int_0^t H_{km}'(t') e^{i\omega_{km}t'} dt', \qquad (1)$$

where $|a_k(t)|^2$ is the probability of finding the system at time t in an energy state E_k, if at $t=0$ when the perturbation is turned on it is known to possess the energy E_m. $H_{km}'(t)$ is the matrix element of the perturbation Hamiltonian connecting the two states, and $\omega_{km} = (E_k - E_m)/\hbar$.

If E_k and E_m are not sharp well-defined energy levels, we must introduce a distribution function $\rho(\omega_{km})$, where $\rho(\omega)d\omega = g(E)dE$ is the probability of finding the energy difference ω_{km} within the range $\omega \pm \frac{1}{2}d\omega$. The total transition probability per unit time to this group of states is

$$w(t) = \frac{d}{dt}\sum_k |a_k(t)|^2 \to \frac{d}{dt}\int_{-\infty}^{\infty}\rho(\omega_{km})d\omega_{km}|a_k(t)|^2, \quad (2)$$

where

$$\int_{-\infty}^{\infty}\rho(\omega_{km})d\omega_{km} = 1.$$

Consider now a case in which the perturbation $H_{km}'(t)$ is a random stationary process. (An example would be the effects of thermal vibrations of a crystal lattice at the site of a single atom.) From (1) it follows that there will be statistical fluctuations in w so that we may define an average transition probability per unit time as

$$\langle w \rangle = \lim_{T \to \infty}\frac{1}{T}\int_0^T w(t)dt$$

$$= \lim_{T \to \infty}\frac{1}{T}\int_0^T dt \frac{d}{dt}\int_{-\infty}^{\infty}\rho(\omega_{km})d\omega_{km}|a_k(t)|^2, \quad (3)$$

where (2) was used. This reduces to

$$\langle w \rangle = \lim_{T \to \infty}\frac{1}{T}\int_{-\infty}^{\infty}\rho(\omega_{km})d\omega_{km}|a_k(T)|^2. \qquad (4)$$

Utilizing Eq. (1) we note that

$$\frac{|a_k(T)|^2}{T} = \frac{1}{\hbar^2 T}\int_0^T\int_0^T H_{km}'(t') \times H_{km}'^*(t'')e^{i\omega_{km}(t'-t'')}dt'dt''.$$

By changing variables so that $t'' - t' = \tau$ and $t' = t$, we

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[1] N. Bloembergen and R. V. Pound, Phys. Rev. **95**, 8 (1954).

[2] See, for instance, L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), 2nd ed., p. 197.