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THE THEORY OF THE EXCITATION OF ATOMIC MERCURY BY ELECTRON IMPACT

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Abstract

The probability of excitation by electron impact of the four P levels (2^1P_1, 2^3P_2, 2^3P_1, 2^3P_0) of Hg has been calculated. It is found that, although with increasing velocities the excitation of two of the triplet levels vanishes compared with that of the singlet, that of the middle triplet level approaches a small constant value (1/25), which can be calculated from the singlet-triplet separation. It is also possible to calculate the number of dispersion electrons f for these transitions by the use of approximate wave functions. Although the absolute magnitude of f is too large by a factor 2, the relative magnitudes are fixed by the singlet-triplet separation and are in good agreement with experiment. An estimate is made of the relative probability of excitation of all four P levels for fairly slow electrons, and these are roughly all of the same order of magnitude, the ratios at 10 volts being 7.0:3.5:1.9:0.4. The variation of the cross sections with voltage are shown in the figure. A brief comparison with experiment is given.

THE theoretical treatment of the problem of the excitation of atoms by electron impact is one which has recently attracted a great deal of interest. Considerable success has been obtained but there are so many different factors entering into the theory that it is difficult to take account of them all. Neglect of any one of these will tend to spoil agreement with experiment under any conditions where this particular feature is of importance. For example, when the velocity of the exciting electrons is high the effect of electron interchange can be neglected and the incident and scattered electrons can be considered as plane waves, but this is not the case for slow electrons. The importance of taking into account electron exchange has been shown by Oppenheimer[1] and Massey and Mohr,[2] the latter authors having worked out the scattering in atomic hydrogen and helium. They obtain very good agreement with the experimental results for the variation with velocity of the effective cross sectional areas corresponding to transitions of the atom to various excited states. Faxen and Holtsmark,[3] Holtsmark[4] and Allis and Morse[5] have considered the scattering of slow electrons by collision with atomic systems, without however, taking into account electron interchange. They find a large variation of the cross section with the velocity, in agreement with experiment.

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[1] J. R. Oppenheimer, Phys. Rev. **32**, 361 (1928).

[2] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. **A132**, 605 (1931).

[3] H. Faxen and J. Holtsmark, Zeits. f. Physik **45**, 307 (1927).

[4] J. Holtsmark, Zeits. f. Physik **48**, 231 (1928); **52**, 485 (1929); **55**, 437 (1929); **66**, 49 (1930).

[5] W. P. Allis and P. M. Morse, Zeits. f. Physik **70**, 567 (1931).

As is well known, the spectrum of a two-electron system, such as helium or mercury, consists of singlets and triplets. If the spectrum is excited optically, then on account of selection rules, the singlet levels do not combine with all of the triplets. If the method of electron impact is used to excite the atom, there results immediately the possibility of exciting the atom into any one of the triplet levels as well as into the singlets. This arises on account of the rearrangement of the electron spins, accomplished by an interchange between an atomic and the incident electrons. The interesting thing to be calculated is the relative excitation probability of the four P levels (viz., 2^1P_1, 2^3P_2, 2^3P_1, 2^3P_0.) of mercury, this being chosen because it is easy to work with experimentally. The following investigation attempts to extend the calculations of Massey and Mohr in two directions. Firstly, according to their calculations, the probability of excitation of the triplet levels becomes vanishingly small as the electron velocity is increased. Actually we shall show that for inter-system lines it approaches a fairly small asymptotic value because the wave functions appropriate to these levels are not entirely antisymmetric in the orbital part alone. Secondly, we shall make an estimate of the relative probabilities of excitation of all three components of the triplet and compare them with that of the singlet. In order to preserve uniformity of notation we shall follow Massey and Mohr as closely as possible.

According to Dirac[6] the first order cross section for excitation of an atom from state n to state m, is given by

$$A_{nm} = 8\pi^3 m^2 k'/h^4 k' \sum_{m_s m_s'} \left| (n,\, k,\, m_s \,|\, V \,|\, m,\, k',\, m_s') \right|^2. \tag{1}$$

Here $kh/2\pi m$ and $k'h/2\pi m$ are the electron velocities before and after impact and V is the interaction energy. m_s and m_s' represent the spin of the incident and scattered electron quantised along some axis, for convenience the same as in the m_L, m_S representation for the atom. The effective cross section for all angles of scattering is then

$$A = \int_0^\pi A_{nm} \sin \delta d\delta$$

where δ is the angle of scattering.

In order to obtain the correct form for the wave functions of the complete system we must take combinations of atomic wave functions and plane waves, representing the incident and scattered electrons. We write

$$\Phi(1,\, 2,\, 3) = e^{ikn_0\cdot r_3}\psi(1,\, 2)^{S_{\alpha_3}}_{S_{\beta_3}} + e^{ikn_0\cdot r_1}\psi(2,\, 3)^{S_{\alpha_1}}_{S_{\beta_1}} + e^{ikn_0\cdot r_2}\psi(3,\, 1)^{S_{\alpha_2}}_{S_{\beta_2}} \tag{2}$$

It is now necessary to consider the wave functions of the mercury atom.

WAVE FUNCTIONS OF THE HG ATOM

The problem of the choice of suitable wave functions for the S and P levels of the mercury atom is one to which only an approximate answer can

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[6] P. A. M. Dirac, Quantum Mechanics p. 179.

be given. We adopt the method of Slater,[7] writing the radial wave function for any electron in the form

$$R(r) = Nr^{n^*-1}e^{-Zr/n^*}[1 + A_1/rZ + A_2/r^2Z^2 + \cdots],$$

where $[Z/n^*]^2$ is the ionization potential for this electron in terms of Rh, and $A_n = -(n^*/2n)[(n^*-n)(n^*-n+1)-l(l+1)]A_{n-1}$. The radius r is measured in terms of a_0, the radius of the first Bohr orbit in hydrogen. In our problem we retain terms up to A_1. We adopt the value $Z=1.65$ for the s electrons in the ground state, 0.35 being Slater's estimate as to how much the electrons shield each other, and $Z=2$, $Z=1$ for the s and p electrons respectively in the excited P states. For the ionization potentials we take 10.4, 18.9[8] and 5.3 volts respectively, the last being chosen to give about the correct position of the four P levels. On substituting these values and introducing the angle variables we find for the three types of wave function

$$\begin{aligned}
\psi(s, S) &= R_{00}(r)/(4\pi)^{1/2} = (1.51/(4\pi)^{1/2})r^{0.87}e^{-0.88r}(1 - 0.92/r),\\
\psi(s, P) &= R_{01}(r)/(4\pi)^{1/2} = (3.03/(4\pi)^{1/2})r^{.69}e^{-1.18r}(1 - 0.50/r),\\
\psi(p, P) &= R_{01}(r)P_1{}^m(\cos\theta)e^{im\phi}\\
&= (0.421(3/4\pi(1 + m)!)^{1/2}r^{0.60}e^{-0.62r}(1 + 0.83/r)P_1{}^m(\cos\theta)e^{im\phi}.
\end{aligned}$$

To satisfy the antisymmetrical condition for the complete wave functions (i.e., inclusive of spin) it is necessary to take combinations of these simple functions. Houston[9] has shown that the S level can be written

$$\psi_S(1, 2) = R_{00}(1)R_{00}(2)1/2^{1/2}(S_{\alpha_1}S_{\beta_2} - S_{\alpha_2}S_{\beta_1}), \tag{3A}$$

and the four P levels

$$\psi_{PjM} = \sum_{i=1}^{4} a_{ijM}\phi_{ijM} \tag{3B}$$

and he gives formulae for the coefficients a. Here M is the component of j along some slight external field, assumed to remove degeneracy, and

$$\begin{aligned}
\phi_{1M}(1, 2) &= 2^{-1/2}[P_0{}^0(1)R_{01}(1)P_l{}^M(2)R_{11}(2)e^{iM\phi_2}\\
&\quad + P_0{}^0(2)R_{01}(2)P_l{}^M(1)R_{11}(1)e^{iM\phi_1}]2^{-1/2}(S_{\alpha_1}S_{\beta_2} - S_{\alpha_2}S_{\beta_1}),\\
\phi_{2M}(1, 2) &= 2^{-1/2}[P_0{}^0(1)R_{01}(1)P_l{}^{M-1}(2)R_{11}(2)e^{i(M-1)\phi_2}\\
&\quad - P_0{}^0(2)R_{01}(2)P_l{}^{M-1}(1)R_{11}(1)e^{i(M-1)\phi_1}]S_{\alpha_1}S_{\alpha_2},\\
\phi_{3M}(1, 2) &= 2^{-1/2}[P_0{}^0(1)R_{01}(1)P_l{}^M(2)R_{11}(2)e^{iM\phi_2}\\
&\quad - P_0{}^0(2)R_{01}(2)P_l{}^M(1)R_{11}(1)e^{iM\phi_1}]2^{-1/2}(S_{\alpha_1}S_{\beta_2} + S_{\alpha_1}S_{\beta_2}),\\
\phi_{4M}(1, 2) &= 2^{-1/2}[P_0{}^0(1)R_{01}(1)P_l{}^{M+1}(2)R_{11}(2)e^{i(M+1)\phi_2}\\
&\quad - P_0{}^0(2)R_{01}(2)P_l{}^{M+1}(1)R_{11}(1)e^{i(M+1)\phi_1}]S_{\beta_1}S_{\beta_2}.
\end{aligned}$$

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[7] J. C. Slater, Phys. Rev. **32,** 349 (1928); **57,** 36 (1930).

[8] H. N. Russell, Astrophys. J. **70,** 11 (1929).

[9] W. V. Houston, Phys. Rev. **33,** 297 (1929). Alternative schemes may be given corresponding with those of E. Wigner, Gruppentheorie p. 208, J. H. Bartlett Jr. Phys. Rev. **34,** 1247 (1929); **38,** 1623 (1931); and N. M. Gray and N. A. Wills, Phys. Rev. **38,** 248 (1931). A little care is needed to be consistent in the definition of matrix elements and differential operators as they are different in the different schemes.

The coefficients a are given in Table I.

TABLE I.

	$S=0$	$S=1$		
M_J	a_1	a_2	a_3	a_4
1	0.979	0.15	0.15	0
0	0.979	−0.15	0	0.15
−1	0.979	0	0.15	0.15

2^1P_1

1	0.207	0.69	0.69	0
0	0.207	−0.69	0	0.69
−1	0.207	0	0.69	0.69

2^3P_1

	$S=0$	$S=1$		
M_J	a_1	a_2	a_3	a_4
2	0	1	0	0
1	0	−0.707	0.707	0
0	0	−0.41	0.82	−0.41
−1	0	0	0.707	−0.707
−2	0	0	0	1

2^3P_2

0	0	0.577	0.577	0.577

2^3P_0

DISPERSION ELECTRONS

In order to test how good an approximation the radial wave functions are, we have calculated the number of dispersion electrons f per atom[10] for the transitions $1^1S_0-2^1P_1$, $1^1S_0-2^3P_1$. In our notation

$$f=(2\nu/3R)\left[\int_0^\infty R_{00}(r_1)R_{01}(r_1)r_1^2dr_1\int_0^\infty R_{00}(r_2)R_{11}(r_2)r_2^3dr_2\right]^2,$$

ν being the frequency of the radiation associated with these transitions. We find 2.0 and 0.066, while the experimental values are 0.96 and 0.0255.[11] The agreement is satisfactory but shows that the value for a_1 for the level 2^3P_1 is too high, it being 0.207 according to Houston's formula instead of 0.185 from the experimental data. Since the f values are too large by a factor 2 we can expect the cross sections calculated from the same wave functions to be too large by a similar factor and this is what is found. However, as we are interested mainly in relative magnitudes, this is not a serious matter.

Substituting the atomic wave functions (3A) and (3B) in the expression (2) we obtain the wave functions for the complete system. Putting these in (1) for the cross sectional area and summing over the spins, it is found [12]

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[10] See for example R. Ladenburg, Zeits. f. Physik **4**, 451 (1921) and Y. Sugiura, Phil. Mag. **4**, 495 (1927).

[11] R. Ladenburg and G. Wolfsohn, Zeits. f. Physik **65**, 207 (1931).

[12] The physical interpretation of this formula is as follows. The first term represents an electron coming away from the impact with the same spin as that of the incident electron; the second and third terms represent a turning over of the spin, the effect of which is to add or subtract 1 from M. To obtain the formula it is necessary to write out a large number of terms. The reader will have no difficulty in obtaining the result quoted if he will write out in full the following steps.

$$(S,\mathbf{k},S_{\alpha}'\,|\,V\,|\,P,\mathbf{k}',S_{\alpha 3})=\int Vdv\left[\sum P_{123}\psi_s(1,2)e^{i k n_0\cdot r_3}S_{\alpha 3}\right]\left[\sum P_{123}e^{i k' n_1\cdot r_3}S_{\alpha 3}\sum_{i=1}^{4}a_{ij}M\phi_{ij}M\right]^*,$$

$$A_{SPM} = k'/k\left[\left| a_1(F_M - G_M) + a_3 g_M \right|^2 + \left| a_2 g_{M-1} \right|^2 + \left| a_4 g_{M+1} \right|^2\right],$$

where

$$F_M = 2\pi m(2\pi)^{1/2} e^2 a_0^2 h^{-2} \int \phi_{1M}^*(1,\, 2) V \psi_S(1,\, 2) e^{i(kn_0 - k'n_1)\cdot r_3} dv,$$

$$G_M = 2\pi m(2\pi)^{1/2} e^2 a_0^2 h^{-2} \int \phi_{1M}^*(2,\, 3) V \psi_S(1,\, 2) e^{i(kn_0\cdot r_3 - k'n_1\cdot r_1)} dv,$$

$$V = \left(\frac{2}{r_3} - \frac{1}{r_{13}} - \frac{1}{r_{23}}\right),$$

and g_M is the same as G_M except that ϕ_2 is substituted for ϕ_1 in the integrand. These ϕ are just the orbital wave functions, the spin functions being omitted. n_0 and n_1 are unit vectors along the direction of motion of the incident and scattered electrons. To find the effective cross sectional area of the atom we must integrate over all angles of scattering and sum over all values of M. Now, as shown by Massey and Mohr[2], the integrals g_M and G_M are much smaller for $M=0$ than for any other values of M and therefore we can write with sufficient approximation

$$A_{SPM} = (k^1/k)\left[\left| a_1(F_M - G_M) + a_3 g_M \right|^2 + \left| a_2 g_{M-1} + a_4 g_{M+1} \right|^2\right].$$

RELATIVE CROSS SECTIONS FOR FAST AND SLOW ELECTRONS

Several interesting features come immediately out of this formula. For the level 2^3P_1, a_1 is small and for 2^3P_2, 2^3P_0, a_1 is zero. Remembering that g_0 is the only g that counts, we find by using the table that the relative cross sections for these three levels for *slow* electrons are in the ratio 3:5:1 respectively. This conclusion is not quite exact since the excitation potentials are not quite the same for all three. This ratio should be roughly that of the maxima of the peaks for the three triplet levels and since g falls off rapidly with increasing velocities, measurements at any velocity will always weight a higher energy level over a lower. The excitation probability decreases rapidly with increasing velocities and for 30 volts g and G are very small. Hence for *fast* electrons it is only the F term which gives anything, so that, although the 2^1P_1 level still remains strong, the only other one left is 2^3P_1, with intensity about 1/25 that of the former, and this ratio should persist for all higher velocities. This latter conclusion can be clearly seen in the experimental results of Larché[13] on cadmiun and zinc. One would expect quite similar results in the case of mercury. If it were not for the cascade effects the experimental value for the number of dispersion electrons would fix the relative cross sections for fast electrons for 2^1P_1 to 2^3P_1 at 34:1.

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where $\sum P_{123}$ means sum over the permutations of electrons 123 as exhibited in Eq. (2). On account of the spin integration the only non-vanishing terms are those from ϕ_1 and ϕ_3 and the contribution of this matrix component to the cross section (1) is $(k'/2k)\left|a_1(F_M - G_M) + a_3 g_M\right|^2$. The component $(S_{\beta_3};\, S_{\beta_3})$ gives a similar amount and $(S_{\alpha_3};\, S_{\beta_3})$, $(S_{\beta_3};\, S_{\alpha_3})$ the second and third terms respectively.

[13] K. Larché, Zeits. f. Physik **67**, 440 (1931).

RATIO OF SINGLET TO TRIPLET FOR INTERMEDIATE SPEEDS

In order to obtain an idea of the relative magnitude of the singlet to triplets for slower electrons it is necessary to evaluate the various integrals. The integration over the angular coordinates is exactly the same as that explained by Massey and Mohr.[2] While it is possible to obtain F satisfactorily g and G are very complicated. In the first place the nodes in the wave functions are of importance. Moreover, it is necessary to consider at least the first two terms in the expansion of $1/r_{12}$ in associated Legendre polynomials. The simplest type of integral occuring is

$$\int_0^\infty \int_0^\infty r_1{}^a e^{-br_1}(1 + c/r_1) J_{3/2}(kr_1)\gamma_\nu(r_1, r_2) r_2{}^d e^{-fr_2}(1 + g/r_2) J_{1/2}(k'r_2) dr_1 dr_2,$$

where $\gamma_\nu(r_1, r_2)$ is of the form $r_1{}^\nu/r_2{}^{\nu+1}$ or $r_2{}^\nu/r_1{}^{\nu+1}$ (ν integer), according as r_2 or r_1 is the greater. The only possible method of evaluating the integrals seemed to be to choose a velocity and then evaluate them numerically. When this is done there is still the integration over δ. Only rough accuracy therefore is claimed.

To obtain some idea of the physical meaning of the fact that although F decreases only slowly with velocity, G and g decrease rapidly, we may roughly describe the state of affairs as follows. F measures the chance that an electron, represented as a plane wave of a certain wave-length and extending from $+\infty$ to $-\infty$ through the atom, should change over into another plane wave of slightly different wave length, also extending from $+\infty$ to $-\infty$ but moving in a different direction. If the angle between the directions of motion of the two electrons is small the two waves are nearly the same, and there is quite a good chance that the influence of the atom will cause the transition. Directly the angle increases the waves differ appreciably and the chance of transition decreases rapidly. We see now why most of the scattered electrons are not deviated much from their original direction and this is particularly the case at high velocities. G and g represent quite a different effect; their interpretation is that an incident plane wave should be changed over into an atomic wave function and at the same time an atomic wave function be changed over into a scattered plane wave. This is easy when the wave-lengths of the electrons (i.e., the electron velocity small) are greater than the diameter of the atom but it becomes increasingly difficult as the electrons are speeded up, and directly there are two or three wave-lengths in atomic dimensions G and g drop nearly to zero.

COMPARISON WITH EXPERIMENT

The general behavior of the excitation probabilities is shown in Fig. 1. The agreement with the experimental values is good although there are no really satisfactory measurements available. I have to thank Professor J. T. Tate for the information that the relative probabilities of $2^3P_1:2^3P_2:2^1P_1$ are quite materially functions of the electron speed and at 10 volts are in the ratio 2.26:3.5:6.6 (the calculated values being about 1.9:3.5:7.0). The probability of 2^3P_0 is very small indeed (we find 0.4). Moreover at this energy 2^1P_1 is increasing while the others are decreasing. These measurements apply only to those electrons which are not deviated much from their forward path by impact. Whitney[14] and Foard[15] have also made measurements on the energy losses in mercury vapor and their experimental results are in good agreement with our conclusions. Foard succeeded in resolving the 4.9 and 5.5 groups but only for primary voltages of about 6 volts. Referring to Fig. 1 it is seen that this is the most suitable region for resolution, the losses being not very different and quite large and the 6.7 loss not present at all. Whitney did not attempt to resolve the triplets but grouped them all together. His curves for the variation of cross section with voltage agree very well in character with ours but seem to attach more importance to the triplet levels at low voltages than we do. However the measurements are so difficult that there is no finality at present. Since we have considered only first order cross sections the agreement is extremely good. As far as the absolute magnitude of the cross section is concerned, it seems that the values obtained are too high. The experimental cross section for all types of collision is about $10\pi a_0^2$ at 200 volts and $6\pi a_0^2$ at 400 volts. For the 2^1P_1 level we get $3\pi a_0^2$ at 200 volts and $2\pi a_0^2$ at 400 volts, while it is even greater at smaller velocities. That excitation to one excited level, even though that be easily the most important, should account for $\frac{1}{3}$ or more of the total cross section seems too high an estimate. Apparently the error is due to the use of wave functions with insufficient nodes.

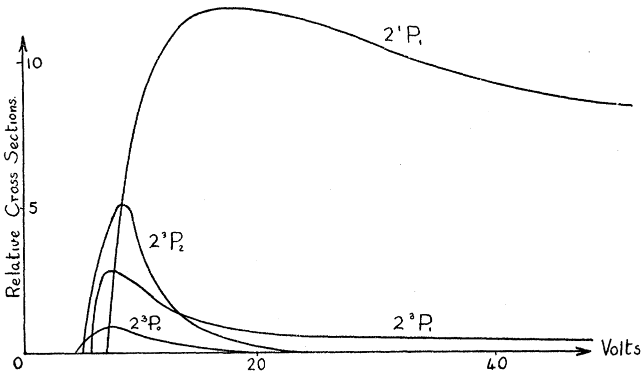

Fig. 1.

In later papers it is hoped to investigate the polarization of the hyperfine components excited by electron impact and also to extend these calculations to higher order cross sections.

I should like to express my thanks to Professor J. H. Van Vleck for many helpful suggestions during the course of this work.

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[14] J. D. Whitney, Phys. Rev. **34**, 923 (1929).

[15] C. W. Foard, Phys. Rev. **35**, 1187 (1930).