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The Exchange Scattering of an Electron by an Atom and Inverse Auger Effect

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The theory of exchange scattering of an electron by an atom given by Mott and Massey is discussed. A new formulation of an approximate treatment of the problem is suggested that leads to a system of differential integral equations similar to the Fock equations for the discrete state of atoms. This method leads to Oppenheimer's result as a first approximation. The resonance scattering arising from the inverse process of auto-ionization (Auger effect) is treated in a phenomenological manner.

I. INTRODUCTION

THE theory of scattering of an electron by an atom including the effect of exchange is first given by Oppenheimer.[1] Another treatment of the problem is given by Mott and Massey[2] which leads to a different result from that of Oppenheimer. Recently this difference in the matrix element for the scattering of an electron by a 2- or more electron atom has been the subject to discussion by a few authors.[3,4] In a recent note[5] the so-called "prior-post discrepancy" arising from this difference has been discussed. The purpose of the present note is to examine the theory of exchange scattering as given by Mott and Massey and to propose a formulation of another approximate theory which gives the total scattering, direct and exchange, in a way analogous to the Fock theory for discrete states and leads to Oppenheimer's result in a first approximation.

II. THEORY OF MOTT AND MASSEY

To simplify the discussion in the following without losing sight of the main features of the problem, we shall consider the scattering by a hydrogen atom of an electron with energy less than that necessary to ionize the atom. The Hamiltonian of the system of two electrons is

$$H(1,2)=-\nabla_1^2-\nabla_2^2-Z/r_1-Z/r_2+1/r_{12}. \qquad (1)$$

In Oppenheimer's theory, out of the last three terms in (1), a perturbation $V(1,2)$ is so defined that the matrix elements in the first Born approximation corresponding to the transition between an initial state with the atom in state 0 and a free electron with momentum k_0, and a final state with the atom in the state n and a free electron with momentum k_n are given by

$$f_n \propto \int\int e^{-i\mathbf{k}_n\cdot\mathbf{r}_2}\psi_n^*(1)\left[-\frac{Z}{r_2}+\frac{1}{r_{12}}\right]\psi_0(1)e^{i\mathbf{k}_0\cdot\mathbf{r}_2}d\mathbf{r}_1d\mathbf{r}_2, \qquad (2)$$

$$g_n \propto \int\int e^{-i\mathbf{k}_n\cdot\mathbf{r}_2}\psi_n^*(1)\left[-\frac{Z}{r_1}+\frac{1}{r_{12}}\right]\psi_0(2)e^{i\mathbf{k}_0\cdot\mathbf{r}_1}d\mathbf{r}_1d\mathbf{r}_2, \qquad (3)$$

for the direct and exchange scattering, respectively.

Before discussing the theory of Mott and Massey for the effect of exchange, let us first treat the problem of two distinguishable electrons and denote by the index 1 the atomic and by the index 2 the incoming electron. A solution of the Schrödinger equation,

$$H(1,2)\psi(1,2)=E\psi(1,2), \qquad (4)$$

is sought in the form

$$\psi(1,2)=\sum_n\psi_n(1)F_n(2), \qquad (5)$$

where the ψ_n's are the complete set of the solutions of the hydrogenic wave equation

$$[\nabla_1^2+Z/r_1+\epsilon_n]\psi_n(1)=0, \qquad (6)$$

the summation sign in (5) indicating summation over both the discrete and the continuous part of the spectrum. The F_n's satisfy the system of equations

$$[\nabla_2^2+(E-\epsilon_m)]F_m(2) = -\int\psi_m^*(1)\left[\frac{Z}{r_2}-\frac{1}{r_{12}}\right]\psi(1,2)d\mathbf{r}_1, \qquad (7)$$

or

$$[\Delta_2^2+(E-\epsilon_m)]F_m(2)=-\sum_n V_{mn}(2)F_n(2),$$

where

$$V_{mn}(2)=\int\psi_m^*(1)\left[\frac{Z}{r_2}-\frac{1}{r_{12}}\right]\psi_n(1)d\mathbf{r}_1. \qquad (7a)$$

To obtain the scattered waves, one seeks solutions $F_m(2)$ that have the following asymptotic forms for large r_2:

$$F_0(2)\rightarrow e^{i\mathbf{k}_0\cdot\mathbf{r}_2}+\frac{e^{ik_0r_2}}{r_2}f_0(\vartheta,\varphi),$$

$$F_m(2)\rightarrow\frac{e^{ik_mr_2}}{r_2}f_m(\vartheta,\varphi), \quad E-\epsilon_m>0, \qquad (8)$$

$F_\mu(2)$ finite at the origin and vanishing exponentially at large r_2, for $E-\epsilon_\mu<0$.

The solution (5) with (8) means that for all states m (discrete in the case considered) of the atom that can be excited by the incoming electron, the incoming electron will emerge and will be described by a spherical

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[1] J. R. Oppenheimer, Phys. Rev. **32**, 361 (1928); G. Wentzel, *Handbuch der Physik* (J. Springer, Berlin, 1933), Vol. 24, No. 1.

[2] W. F. Mott and H. M. Massey, *Theory of Atomic Collisions* (Clarendon Press, Oxford, 1949), 2nd edition, pp. 140, 215, 258.

[3] Bates, Fundaminsky, Leech, and Massey, Trans. Roy. Soc. (London) **A243**, 117 (1950).

[4] D. Layzer, Phys. Rev. **84**, 1221 (1951).

[5] Corinaldesi, Trainor, and Wu, Nuovo cimento **9**, 436 (1952).

wave at large distances. For states (discrete and continuous in this case) for which $E-\epsilon_\mu<0$, the incoming electron 2 is described by $F_\mu(2)$, i.e., it becomes captured by the atom. We shall assume that the asymptotic conditions (8) completely and uniquely determine the F's over the whole range of r_2, and hence also completely and uniquely determine the function $\psi(1,2)$ in (5) over the whole r_1 and r_2 space.

To obtain the effect of electron exchange in which electron 1 goes out and electron 2 is left in the atom, Mott and Massey re-expand the function $\psi(1,2)$ in the alternative form

$$\psi(1,2)=\sum_n\varphi_n(2)G_n(1), \tag{9}$$

where the φ_n's are the complete set of hydrogenic wave functions (we shall denote these by φ's instead of by ψ's for convenience in the argument in the following), and the G_n's are solutions of the system of equations

$$[\nabla_1^2+(E-\epsilon_m)]G_m(1) = -\int \varphi_m^*(2)\left[\frac{Z}{r_1}-\frac{1}{r_{12}}\right]\psi(1,2)d\mathbf{r}_2, \tag{10}$$

or by a system (10a) similar to (7a) but with G's replacing the F's and with the indexes 1, 2 interchanged. The solutions G's are to have the asymptotic forms

$$G_m(1)\to\frac{e^{ikmr_1}}{r_1}g_m(\vartheta,\varphi),\qquad E-\epsilon_m>0,$$

$$G_\mu(1)\to \text{finite at the origin and vanishing exponentially at large } r_1 \text{ for } E-\epsilon_\mu<0. \tag{11}$$

To describe the scattering with the symmetry in the two electrons taken into account, one employs the symmetrized function

$$\begin{aligned}\Psi(1,2)&=\psi(1,2)\pm\psi(2,1)\\&=\sum_n[\psi_n(1)F_n(2)\pm\psi_n(2)F_n(1)].\end{aligned} \tag{12}$$

The function $\psi(2,1)=\sum\psi_n(2)F_n(1)$ represents electron 2 originally in the atom and 1 incident on and scattered by the atom. On re-expanding this $\psi(2,1)$ in the alternative way (9),

$$\psi(2,1)=\sum_n\varphi_n(1)G_n(2), \tag{13}$$

Mott and Massey identify the φ_n's and ψ_n's to be the same set (i.e., covering the same spectrum) and obtain

$$\Psi(1,2)=\sum_n\psi_n(1)[F_n(2)\pm G_n(2)]. \tag{14}$$

Hence, the scattered amplitude is given by the asymptotic amplitude of $F_n(2)\pm G_n(2)$, and from (8) and (11), by

$$f_m\pm g_m,\quad E-\epsilon_m>0. \tag{15}$$

On putting in (7) and (10),

$$\psi(1,2)=\psi_0(1)e^{i\mathbf{k}_0\cdot\mathbf{r}_2},$$

one obtains, to the first approximation,

$$f_m\propto\int\int e^{-i\mathbf{k}_m\cdot\mathbf{r}_2}\psi_m^*(1)\times\left[-\frac{Z}{r_2}+\frac{1}{r_{12}}\right]\psi_0(1)e^{i\mathbf{k}_0\cdot\mathbf{r}_2}d\mathbf{r}_1d\mathbf{r}_2, \tag{16}$$

$$g_m\propto\int\int e^{-i\mathbf{k}_m\cdot\mathbf{r}_2}\psi_m^*(1)\times\left[-\frac{Z}{r_2}+\frac{1}{r_{12}}\right]\psi_0(2)e^{i\mathbf{k}_0\cdot\mathbf{r}_1}d\mathbf{r}_1d\mathbf{r}_2. \tag{17}$$

Before discussing this treatment of Mott and Massey, we shall first note that although the expression (17) for the exchange scattered amplitude has Z/r_2 instead of Z/r_1 as in (3), the two expressions (3) and (17) can be shown to be equal to each other.

We shall now show that the above treatment contains a difficulty connected with the two sets of boundary conditions (8) and (11) for the same function (9),

$$\psi(1,2)=\sum\psi_n(1)F_n(2)=\sum\varphi_n(2)G_n(1). \tag{9}$$

From (9), one obtains

$$\begin{aligned}F_n(2)&=\sum_m\int\psi_n^*(1)G_m(1)d\mathbf{r}_1\cdot\varphi_m(2)\equiv\sum_m a_{nm}\varphi_m(2),\\G_m(1)&=\sum_n\int\varphi_m^*(2)F_n(2)d\mathbf{r}_2\cdot\psi_n(1)\equiv\sum_n b_{mn}\psi_n(1).\end{aligned} \tag{18}$$

From (18), we first note that if the same complete spectrum (regular at the origin and incoming and outgoing waves) is employed for the ψ's in (5) and the φ's in (9), there are in general also incoming waves in $G_m(1)$ coming from the incoming waves in the spectrum of $\psi_n(1)$.

Since the $F_n(2)$'s given by Eq. (7) are determined by the asymptotic conditions (8), Eq. (18) will completely determine the G_n's as defined by the expansion (9). The question is whether the G_n's given by the solution of Eq. (1) with the asymptotic condition (11) are compatible with the G_n's given by (18). Let us denote by $G_n'(2)$ these solutions of (10) subject to (11). These can be written

$$G_m'(2)=-\frac{1}{4\pi}\int\int\frac{e^{ik_m|\mathbf{r}_2-\mathbf{r}_j|}}{|\mathbf{r}_2-\mathbf{r}_j|}\psi_m^*(i)\left[\frac{Z}{r_j}-\frac{1}{r_{ij}}\right]\times\psi(j,i)d\mathbf{r}_id\mathbf{r}_j,\quad E-\epsilon_m>0,$$

$$G_\mu'(2)\ \text{finite at the origin and vanishing exponentially at large } r_2, \text{ for } E-\epsilon_\mu<0. \tag{19}$$

Let us expand $G_n'(2)$ in terms of the complete set of ψ_n's of (6),

$$G_n'(2)=\sum_m b_{nm}'\psi_m(2)+\sum_\mu b_{n\mu}'\psi_\mu(2), \tag{20}$$

where, for example,

$$b_{n\mu}'=\int\psi_\mu^*(2)G_n'(2)dr_2$$

$$=-\frac{1}{4\pi}\int\int\int\psi_\mu^*(l)\frac{e^{ik_n|\mathbf{r}_l-\mathbf{r}_j|}}{|\mathbf{r}_l-\mathbf{r}_j|}\psi_n^*(i)\left[\frac{Z}{r_j}-\frac{1}{r_{ij}}\right]$$

$$\times\psi(j,i)d\mathbf{r}_id\mathbf{r}_jd\mathbf{r}_l. \quad (21)$$

On the other hand, from (18), the coefficient $b_{n\mu}$ of G_n is given by

$$b_{n\mu}=\int\varphi_n^*(1)F_\mu(1)d\mathbf{r}_1,$$

where F_μ is given by (8). Comparison between this and (21) shows that in general

$$b_{n\mu}'\neq b_{n\mu}. \quad (22)$$

Hence, G_n' as given by (10) and (11) are in general not the same as the G_n defined by the alternative expansion (9).

The theory of Mott and Massey has also been given in another form[2,3] which seems not to involve the two sets of asymptotic conditions (8) and (1) separately. The function (14) can be written as

$$\Psi'(1,2)=\sum\Phi_n(2)\psi_n(1), \quad (23)$$

and the Φ's are given by a system of equations similar to (7), with $\psi(1,2)$ in the integrand replaced by $\Psi'(1,2)$, and are subject to the asymptotic conditions

$$\Phi_0(2)\rightarrow e^{i\mathbf{k}_0\cdot\mathbf{r}_2}+\frac{e^{ik_0r_2}}{r_2}\eta_0(\vartheta,\varphi),$$

$$\Phi_n(2)\rightarrow\frac{e^{ik_nr_2}}{r_2}\eta_n(\vartheta,\varphi),\quad E-\epsilon_n>0, \quad (24)$$

$\Phi_\mu(2)$ exponentially decreasing at large r_2, $E-\epsilon_\mu<0$. The solution $\Psi'(1,2)$ so obtained, however, does not ensure the symmetry requirement

$$\Psi'(1,2)=\pm\Psi'(2,1),$$

or

$$\Phi_n(1)=\sum_m\int\psi_n^*(2)\Phi_m(2)d\mathbf{r}_2\cdot\psi_m(1). \quad (25)$$

Apart from this question of satisfying simultaneously both the symmetry requirement (12) or (25) and the two sets of asymptotic conditions (8) and (11), another related point may be raised in this theory. The function (12) or (14), being obtained from (5) and (13) without exchange, corresponds to a Hartree approximation; while an exact theory should correspond to a Fock approximation, i.e., the functions F_n's in (12) should be given by an infinite system of differential-integral equations obtained by putting (12) into (4).

Thus the theory of exchange scattering of Mott and Massey, and the approximation (17) in particular, must be accepted only as a definite approximation, which is, however, different from that made in the usual Born approximation without exchange.

III. A PROPOSED TREATMENT OF EXCHANGE SCATTERING

In view of the difficulty discussed in the preceding section in the treatment of Mott and Massey, a new treatment of the problem is suggested which is somewhat analogous to the theory of Fock for the discrete states of an atom.

Let us consider, for definiteness, the scattering by a hydrogen atom of an electron of energy k_0^2 sufficient to excite the discrete states $0, 1, \cdots, m$ but not sufficient to ionize the atom. The physical condition of the problem is therefore the scattering of one of the electrons with an energy $k_n^2=E-\epsilon_n=k_0^2-(\epsilon_n-\epsilon_0)$, leaving behind the other electron in the state n of the atom. E is the total energy of the system; ϵ_0, ϵ_n are the energies of the initial and the excited state of the atom. To describe this condition of the problem, we shall construct a symmetrized wave function for the system

$$\Psi(1,2)=\sum_{n=0}^{m}[\psi_n(1)\phi_n(2)\pm\psi_n(2)\phi_n(1)], \quad (26)$$

where the ψ's are the wave functions of those discrete states of the hydrogen atom that can be excited with the energy available, and the ϕ's are the wave functions of the incident and scattered electron. On putting (26) into the Schrödinger Eq. (4), one obtains the system $m+1$ differential-integral equations

$$[\nabla_1^2+k_n^2]\phi_n(1)$$

$$=-\frac{Z}{r_1}\phi_n(1)+\sum_{l=0}^{m}\int\psi_n^*(2)\psi_l(2)\frac{1}{r_{12}}d\mathbf{r}_2\cdot\phi_l(1)$$

$$\pm\sum_l\int\psi_n^*(2)\left[-\nabla_2^2-\frac{Z}{r_2}-k_l^2+\frac{1}{r_{12}}\right]\phi_l(2)d\mathbf{r}_2\cdot\psi_l(1)$$

$$=-\sum_{l=0}^{m}V_{nl}(1)\phi_l(1)\pm\sum_{l=0}^{m}\int\psi_n^*(2)\left[\epsilon_n-k_l^2+\frac{1}{r_{12}}\right]$$

$$\times\phi_l(2)d\mathbf{r}_2\cdot\psi_l(1), \quad (27)$$

where $V_{nl}(1)$ is given by an expression similar to (7a), and where $\epsilon_n-k_l^2=\epsilon_l-k_n^2$ on account of the energy conservation $E=k_n^2+\epsilon_n=k_l^2+\epsilon_l$.

We seek solutions that have the following asymptotic behavior:

$$\phi_0(1)\rightarrow e^{i\mathbf{k}_0\cdot\mathbf{r}_1}+\frac{e^{ik_0r_1}}{r_1}\eta_0(\vartheta,\varphi),$$

$$\phi_n(1)\rightarrow\frac{e^{ik_nr_1}}{r_1}\eta_n(\vartheta,\varphi),\quad n=1,\cdots m. \quad (28)$$

The amplitudes η_0, η_n for the elastic and inelastic scattering, being obtained from Eqs. (27) that include the effect of the use of symmetrized wave functions, already contain the direct and the exchange scattering. As the system (27) is a finite number of equations, the solutions ϕ_n can in principle be obtained at least by successive approximation.

The approximation involved in this method is contained in the form (26) for the wave function. It is seen that the function (26) together with (28) satisfies the physical conditions required of the solution. In limiting the hydrogenic wave functions ψ's to only those states $\epsilon_n < \epsilon_m$ where $\epsilon_m \leqslant k_0^2 + \epsilon_0$, the function (1) errs in the regions of the configuration space where both r_1 and r_2 are small. But it is exactly here that the usual Born and Oppenheimer approximations are also bad, since in these approximations the whole wave function $\psi(1, 2)$ in the integrand of Eqs. (7), (10) is replaced by only one term. By finding solutions ϕ's of the system of Eq. (27), the coupling among the various scattered wave ϕ's is better accounted for than in the Born approximation in which the coupling is neglected. The chief interest of this method is perhaps the less ambiguous way in which the exchange effect is included in the scattered waves ϕ's. The total scattering including the effect of symmetry is given by the system of differential integral Eqs. (27), quite analogous to the Fock equations for the discrete states of an atom.

It is of interest to note that if, to a first approximation, one puts on the right-hand side in Eqs. (27)

$$\begin{aligned}\phi_0(r) &= e^{i\mathbf{k}_0\cdot\mathbf{r}},\\ \phi_l(r) &= 0, \quad l \neq 0,\end{aligned} \tag{29}$$

the system of simultaneous equations becomes a system of independent inhomogeneous equations and one obtains, to this approximation,

$$\begin{aligned}\phi_0(1) &\rightarrow e^{i\mathbf{k}_0\cdot\mathbf{r}_1} + \frac{e^{ik_0r_1}}{r_1}(f_0 \pm g_0),\\ \phi_n(1) &\rightarrow \frac{e^{ik_nr_1}}{r_1}(f_n \pm g_n),\end{aligned} \tag{30}$$

where the f_n's are given (2) and g_n by (3). Thus, Oppenheimer's result follows as a first approximation to the method here.

IV. INVERSE AUGER TRANSITION AND RESONANCE SCATTERING

Let us consider the case when the total energy of the system $E = k_0^2 + \epsilon_0$ is just equal to the energy E_a of one of the quasi-stationary, doubly excited states (such as $2s3s$, $3s^2$, etc.) which are subject to the radiationless auto-ionization similar to the Auger transitions in x-rays. In this case there is the possibility of the incoming electron being captured and re-emitted. An exact treatment of the auto-ionization process is difficult; but its inverse process can be treated in an approximate way as follows. When k_0^2 is such that $k_0^2 + \epsilon_0 = E_a$, we shall, instead of the wave function (27), assume the wave function[6]

$$\Psi(1, 2) = \sum_{n=0}^{m} [\psi_n(1)\phi_n(2) \pm \psi_n(2)\phi_n(1)] + \psi_a(1)\phi_a(2) \pm \psi_a(2)\phi_a(1), \tag{31}$$

where $\psi_a(1)$ is again a discrete hydrogen wave function. On putting (31) into Eq. (4), one obtains the following system of $m+2$ differential-integral equations:

$$\begin{aligned}[\nabla_1^2 + k_n^2]\phi_n(1) = &-\sum_{l=0}^{m,\,a} V_{nl}(1)\phi_l(1)\\ &\pm \sum_{l=0}^{m,\,a} \int \psi_n^*(2)\left[\epsilon_n - k_l^2 + \frac{1}{r_{12}}\right]\phi_l(2)d\mathbf{r}_2 \cdot \psi_l(1),\\ &n = 0, 1, \cdots m, a,\end{aligned} \tag{32}$$

where $k_a^2 = E - \epsilon_a$ is negative. The solutions sought are to have the following asymptotic forms:

$$\begin{aligned}\phi_0(1) &\rightarrow e^{i\mathbf{k}_0\cdot\mathbf{r}_1} + \frac{e^{ik_0r_1}}{r_1}\xi_0(\vartheta, \varphi),\\ \phi_n(1) &\rightarrow \frac{e^{ik_nr_1}}{r_1}\xi_n(\vartheta, \varphi), \quad n = 1, 2, \cdots m,\end{aligned} \tag{33}$$

$\phi_a(1)$ decreasing exponentially at large r_1.

The difference of the amplitudes ξ's in (31) from the η's in (29) represent the resonance scattering arising from the possibility of the inverse process of the Auger transition. When the differential cross sections are studied at various energies k_0^2, there would be an anomaly when $k_0^2 + \epsilon_0 = E_a$, the energy of one of the doubly excited states, corresponding to the differential cross sections passing from $|\eta(\vartheta, \varphi)|^2$ to $|\xi(\vartheta, \varphi)|^2$ and back to $|\eta(\vartheta, \varphi)|^2$.

Experimentally, one may study this resonance effect by measuring the scattering at a fixed angle (preferably a large angle) for a continuous range of electron energy. The question as to what the theoretical energies E_a are cannot be answered in this "phenomenological" treatment given above. But in the sense of successive approximations, one may perhaps locate the positions of the doubly excited states by a separate calculation based on the variational principle, for example.

The writer has had many discussions of the problem with Dr. E. Corinaldesi, Dr. L. Trainor, and Dr. E. Bauer, and is particularly indebted to Dr. S. T. Ma and Dr. T. D. Lee for clarifying discussions.

Note added in proof:—In a recent paper [Proc. Roy. Soc. (London) **A212**, 512 (1952)] G. A. Erskine and H. W. S. Massey calculate the excitation cross section for the $2S$ state of hydrogen in an approximation quite similar to that of Sec. III above, except that in the function (26) only two states, namely, the initial and the final, are included.

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[6] This approximate treatment is not free from ambiguity in that, for the doubly excited state such as $2s3s$, it is not clear whether one should put ϕ_a equal to ψ_{2s} or to ψ_{3s}. One may, of course, include two terms in (31), namely,

$$\psi_{2s}(1)\phi_a(2) \pm \psi_{2s}(2)\phi_a(1) + \psi_{3s}(1)\phi_b(2) \pm \psi_{3s}(2)\phi_b(1).$$