

Low-Energy Electron-Atom Scattering: The Case of Near Degeneracy

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We study low-energy elastic electron scattering from an atomic or molecular target for the case where the initial state of the target is close in energy to target states of opposite parity. We show that under these circumstances there is a range of small scattering angles in which the angular distribution varies rapidly. Experimental tests are suggested.

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The low-energy interaction of an electron with an atom or molecule is a subject of long standing, from both a physical and a mathematical point of view. From a theoretical perspective it can be regarded as belonging in part to the quantum theory of long-range forces. As is well known, and expected on classical grounds, the leading term at large distances in the effective (or "optical") potential describing the interaction of an electron 1 with a neutral atom in its ground state is given by

$$V_{\text{dip}}(r_1) = -e^2\alpha_E/2r_1^4, \quad (1)$$

where α_E is the static electric polarizability of the atom. Equation (1) holds even if relativistic effects are included, provided that α_E is appropriately defined.¹ For most cases of interest it suffices to calculate α_E from the familiar nonrelativistic formula

$$\alpha_E = -\frac{2}{3} \sum_n \langle 0|\mathbf{d}|n\rangle \cdot \langle n|\mathbf{d}|0\rangle / (W_0 - W_n), \quad (2)$$

where \mathbf{d} is the electric-dipole operator ($\mathbf{d} = e\mathbf{r}$ for a one-electron atom), the sum is over a complete set of eigenfunctions $|n\rangle$ of the nonrelativistic atomic Hamiltonian with eigenvalues W_n , and $|0\rangle$ denotes the initial state of the target, which for simplicity is taken to be an S state. In practice, the asymptotic form (1) is used only to compute the partial-wave phase shifts for $l \geq 2$, by use of the Born approximation for $\tan\delta_l$. For smaller values of l , especially $l=0$, it is necessary to do better, e.g., by numerical solution of the

Schrödinger equation or by use of a variational principle; there is an extensive literature devoted to this subject.²

This approach fails when the initial state of the target is very close in energy to other target states of opposite parity, even if the electron kinetic energy is large compared to the energy difference between the states. The scattering is then not adequately described by a potential for any partial wave. This situation was considered long ago and a "close-coupling method" was developed³ to deal with it. That method focuses on the calculation of individual partial waves. For the differential elastic-scattering cross section at small angles, in the degenerate case that we study here, there is a singularity in the scattering angle $f(p, \cos\theta)$ at small θ whose calculation would require the summation of an infinite number of partial waves.⁴ In this Letter, we show that the exact behavior of the elastic-scattering amplitude at small angles can be obtained by a careful treatment of the second Born approximation to f . Previous discussions have not considered the differential cross sections for elastic scattering and so have not found the singularity that we discuss.⁵

For simplicity let us ignore spin and exchange and consider a neutral target involving a valence electron 2 in an initial S state, with wave function $\phi_0(r_2)$. Let $\phi_1^m(r_2)$ ($m=0, \pm 1$) denote the wave functions of a nearby triplet of P states. The contribution $f_P^{(2)}$ of this triplet to $f^{(2)}$, the second Born approximation⁶ to the elastic-scattering amplitude f , is given by

$$f_P^{(2)} = -\frac{m}{2\pi} \int \frac{d^3k}{(2\pi)^3} \frac{\langle \mathbf{p}', \phi_0 | U | \mathbf{k}, \phi_1^m \rangle \langle \mathbf{k}, \phi_1^m | U | \mathbf{p}, \phi_0 \rangle}{W_0 + p^2/2m - W_1 - k^2/2m + i\epsilon}. \quad (3)$$

Here $|\mathbf{p}\rangle$, $|\mathbf{p}'\rangle$, and $|\mathbf{k}\rangle$ denote initial, final, and intermediate plane-wave states of the incident electron 1, respectively, and

$$U = e^2/r_{12} - e^2/r_1 \quad (4)$$

is the sum of the Coulomb interaction of 1 with the target electron 2 and with the nucleus.⁷

One can see most simply the problems that arise when $W_1 - W_0$ is small by making not only the dipole approxi-

mation, i.e., replacing U by its asymptotic form for r_1 much larger than r_2 ,

$$U \rightarrow U_{\text{dip}} = e^2 \mathbf{r}_1 \cdot \mathbf{r}_2 / r_1^3, \quad (5)$$

but also making the adiabatic approximation, i.e., neglecting the projectile excitation energy $(k^2 - p^2)/2m$ relative to the target excitation energy $W_1 - W_0$. Then (3) reduces to

$$f_P^{(2)} \rightarrow (f_P^{(2)})_{\text{dip,ad}} = -(m/2\pi) \langle \mathbf{p}' | V'_{\text{dip}} | \mathbf{p} \rangle, \quad (6a)$$

where

$$V'_{\text{dip}} = -e^2 \alpha'_E / 2r_1^4. \quad (6b)$$

Here α'_E is the contribution of the P -state triplet to α_E :

$$\alpha'_E = e^2 (4m/\Delta) r_P^2, \quad (6c)$$

where r_P^2 is a mean square transition length

$$r_P^2 = \sum_m \langle \phi_0 | \mathbf{r}_2 | \phi_m \rangle \cdot \langle \phi_m | \mathbf{r}_2 | \phi_0 \rangle / 3 \quad (7)$$

and

$$\Delta = 2m(W_1 - W_0). \quad (8)$$

The fact that α'_E becomes large if Δ becomes small is, of course, a signal that the approximations involved break down in the limit $\Delta \rightarrow 0$.

To study the case of near degeneracy, i.e., small Δ , we investigate the behavior of the function $f_P^{(2)}$ without making the adiabatic approximation. We focus on the region where the momentum transfer Q is small compared to the incident momentum p , corresponding to small scattering angles, and the excitation

energy $W_1 - W_0$ is small compared to the incident energy $p^2/2m$. To be precise, we shall assume that

$$Q^2 \ll p^2, \quad \Delta \ll p^2, \quad (9)$$

without for the moment putting any restrictions on the relative magnitude of Q^2 and Δ . On replacing U by U_{dip} in (3) we get,⁸ with a_0 the Bohr radius,

$$f_P^{(2)} \rightarrow (f_P^{(2)})_{\text{dip}} = -(2/\pi^2) (r_P/a_0)^2 K(Q, \Delta; p), \quad (10)$$

where $\mathbf{Q} = \mathbf{p} - \mathbf{p}'$ and the function K is defined by

$$K = - \int d^3k (\mathbf{q} \cdot \mathbf{q}' / q^2 q'^2) (p^2 - \Delta - k^2 + i\epsilon)^{-1}, \quad (11)$$

with $\mathbf{q} = \mathbf{p} - \mathbf{k}$ and $\mathbf{q}' = \mathbf{k} - \mathbf{p}'$. Because p^2 is larger than Δ , the integral has both a real and an imaginary part, corresponding to a dispersive and an absorptive contribution to $f_P^{(2)}$.

On use of the identity $(x + i\epsilon)^{-1} = P(1/x) - i\pi\delta(x)$, one finds that $\text{Re}K$, given by the principal-value integral, is regular in the region defined by (9) and has a finite value in the limit $Q^2 \rightarrow 0$, $\Delta \rightarrow 0$, given by

$$\text{Re}K(0, 0; p) = -\pi^3/2p. \quad (12)$$

However, the function $\text{Im}K$, given by the delta-function integral, is singular for $Q^2 \rightarrow 0$ if $\Delta = 0$ and therefore must be examined more carefully. The integral for $\text{Im}K$ may be evaluated analytically, with the result that

$$\text{Im}K = -(\pi^2/p) \{ \ln[(p + k_0)^2/\Delta] - (Qp/A_0) \ln[(A_0 + k_0Q)/\Delta] \}, \quad (13)$$

where $k_0 = (p^2 - \Delta)^{1/2}$ and $A_0 = (\Delta^2 + k_0^2 Q^2)^{1/2}$. The function given by (13) depends sensitively on the value of the ratio Q^2/Δ . On restricting ourselves to the region defined by (9) we find, for $Q^2/\Delta \gg \Delta/p^2$,

$$\text{Im}K \approx -(\pi^2/2p) \ln(4p^2/Q^2), \quad (14)$$

and, for $Q^2/\Delta \ll \Delta/p^2$,

$$\begin{aligned} \text{Im}K &\approx -(\pi^2/p) \ln[(p + k_0)^2/\Delta] \\ &\approx -(\pi^2/p) \ln(4p^2/\Delta). \end{aligned} \quad (15)$$

Note that the constraint used in arriving at (14) still allows the argument of the logarithm to be very small and hence $\text{Im}K$ to be relatively large, since it requires only that Q^2/p^2 be large compared to $(\Delta/p^2)^2$.

The above analysis suggests that in the region where $Q^2/p^2 \ll 1$ and (14) holds we consider an approximation \tilde{f} to the amplitude f which is the sum of three terms,

$$\tilde{f} = f_0 + [g^{(2)}]_{l \neq 0} + [(f_P^{(2)})_{\text{dip}}]_{l \neq 0}. \quad (16)$$

Here the first term $f_0 = \exp(i\delta_0) \sin\delta_0/p$ is the exact

$l=0$ amplitude; the second term is the contribution to $f^{(2)}$ arising from intermediate atomic states which are not close in energy to the initial target state, calculated in the dipole-adiabatic approximation; and the last term is the value of $(f_P^{(2)})_{\text{dip}}$ obtained by using the approximation to $\text{Im}K$ given by (14). The subscript $l \neq 0$ indicates that the spherical average of the quantity in question is to be subtracted. This is necessary in order to avoid double counting, since f_0 already contains the $l=0$ part of the second Born approximation.

The $l \neq 0$ part of the purely real amplitude $g^{(2)}$ is

$$[g^{(2)}]_{l \neq 0} = -\frac{m}{2\pi} \int d^3r [j_0(Qr) - j_0^2(pr)] V''_{\text{dip}}(r), \quad (17)$$

where $j_0(x) = \sin x/x$, $V''_{\text{dip}} = -e^2 \alpha''_E / 2r^4$, and α''_E is a reduced polarizability defined by $\alpha''_E = \alpha_E - \alpha'_E$. A short calculation shows that

$$[g^{(2)}]_{l \neq 0} = (\pi \alpha''_E / 12a_0) (4p - 3Q). \quad (18)$$

To find $[\text{Im}K]_{l \neq 0}$, we calculate the angular average of

$\text{Im}K$ from (13) and find that

$$[\text{Im}K]_{l \neq 0} = (\pi^2/p) \{ (Qp/A_0) \ln[(A_0 + k_0 Q)/\Delta] - \ln(4p^2/\Delta) + \frac{1}{2} + O(\Delta/p^2) \}. \quad (19)$$

For $Qp \gg \Delta$ this reduces to

$$[\text{Im}K]_{l \neq 0} \approx -(\pi^2/2p) \ln[(4p^2/Q^2) - 1]. \quad (20)$$

The quantity $[\text{Re}K]_{l \neq 0}$ has no $\ln(p^2/Q^2)$ term, consistent with (13); calculation shows that the product $p[\text{Re}K]_{l \neq 0}$ is of order Q^2/p^2 and therefore negligible for $Q^2 \ll p^2$. As $Q^2 \rightarrow 0$, the right-hand side of (20) has the same singularity as that of (14), since that singularity comes from the long-range part of the interaction and is not affected by the removal of any finite number of partial waves.

Another way to obtain (14) is from the partial-wave expansion for $f(p, \cos\theta)$. If one makes the dipole approximation in the computation of the partial-wave amplitudes $f_l(p)$, then in the case of exact degeneracy and with neglect of coupling to atomic states with different energies, the corresponding quantities $\tilde{f}_l(p)$ can

be computed exactly, since in diagonalized form the effective scattering potential is just proportional to $1/r^2$. This was done long ago by Seaton.³ However, Seaton did not discuss the behavior of the associated sum $\tilde{f}(p, \cos\theta)$. It is straightforward to show that if each $\tilde{f}_l(p)$ is expanded in powers of r_p/a_0 and only the leading term is retained, this sum reproduces the logarithmically singular term in (14). Higher-order terms in r_p/a_0 represent the contributions of higher-order Born approximations, but these are not singular for small θ .

We are thus led to study an approximation to the differential cross section given by

$$d\sigma/d\Omega \approx |\tilde{f}|^2 = |\text{Re}\tilde{f}|^2 + |\text{Im}\tilde{f}|^2, \quad (21)$$

where

$$\text{Re}\tilde{f} = p^{-1} [\cos\delta_0 \sin\delta_0 + (\pi\alpha_E''/3a_0)p^2(1 - 3Q/4p) + p(\text{Re}K)_{l \neq 0}] \quad (22)$$

and

$$\text{Im}\tilde{f} = p^{-1} [\sin^2\delta_0 + C(Q, p)], \quad (23)$$

with

$$C(Q, p) = (r_p/a_0)^2 [\ln(4p^2/Q^2) - 1]. \quad (24)$$

Note that $C(Q, p)$ depends only on the scattering angle, not on the energy.

To be concrete, let us consider experiments for which the kinetic energy $T = p^2/2m$ is of order 1 eV and the scattering angle θ is of the order of 0.1 rad. With $\alpha_E'' \sim a_0^3$, the second term in (22) is then of order 0.1 and we neglect it, together with the third term, relative to the first term in (22). However, with $r_p/a_0 \sim 1$, the quantity $C(Q, p)$ is of order $\ln(4p^2/Q^2) \sim \ln 4/\theta^2 = \ln 400 \approx 6$, and thus the second term in (23) will dominate the first term. The cross section in this region will then be roughly given by⁹

$$\frac{d\sigma}{d\Omega} \approx p^{-2} [\sin^2\delta_0 + 2 \sin^2\delta_0 C(Q, p) + C^2(Q, p)] \quad (25)$$

and have the strong angular dependence predicted by (24).

We see that in order to make the contribution from the quasidegenerate states large compared to that of other states we need to consider kinetic energies which are large compared to $W_1 - W_0$ but not large compared to the other dipole-connected states. There are several circumstances in which this condition can be satisfied. One involves electron scattering from H or H-like ions in the metastable $2S$ state, which is split from the $2P_{1/2}$

state by the Lamb shift, of order 4×10^{-6} eV. In this case the condition $Qp \gg \Delta$, equivalent to $\theta \gg \Delta/2mT$ for small angles, is easy to satisfy. If, for example, $\theta = 1^\circ$, $\ln(4p^2/Q^2) \approx 9$, so that there is a substantial enhancement and we only need $T \gg 10^{-4}$ eV. Another case involves electron scattering from an excited S state of an alkali atom such as Na. The difference $W(4s) - W(4p)$ is 0.6 eV so that for $\theta = 10^\circ$ we need $T \gg 3$ eV while $\ln(4p^2/Q^2) \approx 5$.

In order to observe convincingly the effect in question, one must be able to distinguish elastic scattering from inelastic excitation of the nearby P state, a process which may have a differential cross section which is much larger and which may vary more rapidly with angle than the elastic differential cross section. In both of the above-mentioned cases the elastic scattering should be distinguishable from inelastic scattering to the P state, through the observation of the prompt photon from the decay of the P state.

A third case which would seem favorable for observing the effect in question is elastic scattering from a polar molecule. Here the dipole matrix element comes from a transition between a $J=0$ and a $J=1$ rotational state and $W_1 - W_0 \sim 10^{-3}$ eV, so that for $\theta = 1^\circ$ we only need $T \gg 0.05$ eV. However, for scattering from a molecule it appears more difficult to distinguish elastic scattering from rotational excitation.

Finally, let us consider the extent to which the effect in question can be usefully described by a "potential."¹⁰ One can see from (12) and (13) that if a po-

tential \mathcal{V} is defined by the Fourier transform

$$\mathcal{V} = -\frac{2\pi/m}{(2\pi)^3} \int d^3Q \exp(-i\mathbf{Q}\cdot\mathbf{r}) f^{(2)}(Q, p; \Delta),$$

then \mathcal{V} is both complex and strongly dependent on energy. The behavior of \mathcal{V} for large r depends on the behavior of $f^{(2)}$ for $Q \rightarrow 0$, with p fixed. For $\Delta = 0$ and $p = 0$, we get $(f_p^{(2)})_{\text{dip}} \propto ip^{-1} \ln(Q/p)$ so that $\mathcal{V} \propto i/pr^3$ for large r . Thus the introduction of a potential does not seem to be useful in the present context.

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⁴The situation that a large or infinite number of the close-coupling partial-wave amplitudes need to be summed to give accurate results has occurred in other applications. See, e.g., O. H. Crawford and A. Dalgarno, J. Phys. B **4**, 494 (1971).

⁵A summary of much of the theoretical work on scattering of electrons by polar molecules is given by D. W. Norcross and L. A. Collins, Adv. At. Mol. Phys. **18**, 341 (1982).

⁶There is also a first-Born-approximation term, $f^{(1)}$, coming from U ; however, $f^{(1)}$ is negligible compared to $f^{(2)}$ in the region of interest to us.

⁷We have also studied this problem using the covariant methods of Ref. 1, thereby including the contributions arising from transverse-photon exchange; for $p/m \ll 1$ the results coincide with those given in this paper.

⁸The difference $U - U_{\text{dip}}$ has two parts. One, for $r_1 > r_2$, involves higher multipoles than the first and makes no contribution to $f_p^{(2)}$. The other, for $r_2 > r_1$, gives rise to a contribution which, like $f^{(1)}$, is negligible for small values of Q .

⁹This formula is only schematic. Before applying it to, e.g., e^- -H scattering, one must make the usual modifications to take into account exchange, by introducing singlet and triplet phase shifts, etc.; see Ref. 2.

¹⁰A study of the second Born approximation for charge-atom scattering in terms of a potential has been made by D. A. Kirzhnits and F. M. Pen'kov, Zh. Eksp. Teor. Fiz. **85**, 80 (1983) [Sov. Phys. JETP **58**, 46 (1983)].