# Polarization in distant Coulomb collisions of charged particles with atoms*

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The inelastic collisions of a heavy fast particle of charge $Z_1e$, incident at an impact parameter $b$, with an electron bound in an atom isotropically and harmonically is considered. The "atom" is treated by quantum mechanics, extending an earlier classical calculation by Ashley, Ritchie, and Brandt. A multipole expansion of the Coulomb interaction for distanct collisions is used. Two methods are employed to calculate $Z_1^3$ contributions to the mean energy loss and the excitation probabilities due to dipole and quadrupole terms in the multipole expansion. In one method the dipole interaction is taken into account exactly by applying the quantum formalism of the forced harmonic oscillator, and the quadrupole interaction is treated as a first-order perturbation. The second method of calculation employs both dipole and quadrupole interactions as time-dependent perturbations to second order on the free harmonic oscillator. The energy loss calculated for a particle incident on a straight-line trajectory agrees with the classical calculation. Reasons for this agreement are given. Simplifications of the calculation owing to time-reversal symmetry considerations and selection rules for the harmonic oscillator are discussed. Comments are made concerning the relative importance of distant and close collisions at high and low impact velocities.

## I. INTRODUCTION

According to first-order perturbation theory, the probability that a fast heavy particle of charge $Z_1e$ will excite or ionize an atom in a collision is proportional to $Z_1^2$. Recent measurements of the mean energy loss[1-3] and of inelastic-collision cross sections[4,5] have shown appreciable departures from this simple relationship and have led to an examination of the theoretical corrections to the $Z_1^2$ law. An instructive classical calculation[6] of the $Z_1^3$ contribution to the energy loss (stopping power) has been made, using an isotropic harmonic oscillator as a model for an electron bound in an atom.[7]

This paper treats the same problem but gives a fully quantal rather than classical account of the "atom", i.e., the isotropic harmonic oscillator. Since the incident charged particle is described by impact-parameter methods, the present calculation is appropriately characterized as semiclassical. Like its predecessor,[6] this calculation deals only with the so-called distant collisions, corresponding to large impact parameters and permitting a multipole expansion in inverse powers of the projectile-target distance. Both calculations involve an exact evaluation of the dipole ($E1$) contribution to the energy loss and a perturbation treatment of the quadrupole ($E2$) contribution. All higher multipole terms are neglected. In many ways, the theory resembles that of multiple nuclear Coulomb excitation, but there are significant distinctions attributable to the difference between the collective model of the nucleus and the single-particle model of the atom.[8]

Section II provides the theoretical formalism leading to an expression for the energy loss which is identical with the classical result, but the same methods also permit the evaluation of excitation probabilities and inelastic-collision cross sections, which have no place in a wholly classical approach. The general formulas are specialized in Sec. III to the particular case of an incident charged particle moving uniformly on a straight-line trajectory. The theory of Secs. II and III, which treats the dipole interaction exactly, is compared with straightforward perturbation theory in Sec. IV. A discussion of the model and its possible extension concludes the paper (Sec. V).

## II. GENERAL THEORY

The Coulomb interaction between a classical particle of charge $Z_1e$ at position $\vec{\mathbf{R}}(t)$ with coordinates $X(t)$, $Y(t)$, $Z(t)$, and an electron located at position $\vec{\mathbf{r}}(x,y,z)$, measured from the atomic nucleus as the origin, is given by

$$V(t) = -\frac{Z_1e^2}{|\vec{\mathbf{R}}(t)-\vec{\mathbf{r}}|} = -Z_1e^2\left[\frac{1}{R(t)}+\frac{\vec{\mathbf{R}}(t)\cdot\vec{\mathbf{r}}}{[R(t)]^3} +\frac{1}{2}\left(\frac{3[\vec{\mathbf{R}}(t)\cdot\vec{\mathbf{r}}]^2}{[R(t)]^5}-\frac{r^2}{[R(t)]^3}\right)+O\left(\frac{r^3}{R^4}\right)\right] \tag{1}$$

for $R(t)\gg r$. The monopole, dipole, and quadrupole terms are of order $1/R$, $r/R^2$, $r^2/R^3$, respectively.

Assuming that the charged particle remains out-

side the "atom" during the course of its motion, the dipole potential may be regarded as giving rise to a spatially uniform force which varies in time in a specified manner. The Hamiltonian of the system is conveniently expressed as the sum

$$H = H_1(t) + V_2(t) \tag{2}$$

of an "unperturbed" part,

$$H_1(t) = H_0 + V_1(t) = \frac{p_x^2 + p_y^2 + p_z^2}{2\mu} + \tfrac{1}{2}\mu\omega^2(x^2+y^2+z^2) - \frac{Z_1 e^2}{[R(t)]^3}[X(t)x + Y(t)y + Z(t)z], \tag{3}$$

and a "perturbation",

$$V_2(t) = -\frac{Z_1 e^2}{2}\left(\frac{3[\vec{\mathbf{R}}(t)\cdot\vec{\mathbf{r}}]^2}{[R(t)]^5} - \frac{r^2}{[R(t)]^3}\right). \tag{4}$$

The monopole term has been omitted from the Hamiltonian, since it does not affect the transition probabilities as long as $R(t) \gg r$ is valid for all $t$ and all pertinent values of $r$. The Hamiltonian $H_1(t)$ is that of a forced isotropic harmonic oscillator. The equation of motion of such an unperturbed, albeit time dependent, quantum system may be solved exactly by separation of variables in the Cartesian coordinates $x = x_1, y = x_2, z = x_3$.

The lowering and raising operators,

$$a_j = \left(\frac{\mu\omega}{2\hbar}\right)^{1/2}\left(x_j + i\frac{p_j}{\mu\omega}\right),$$

$$a_j^\dagger = \left(\frac{\mu\omega}{2\hbar}\right)^{1/2}\left(x_j - i\frac{p_j}{\mu\omega}\right),$$

for the three independent linear oscillators satisfy the commutation relations

$$a_j a_k^\dagger - a_k^\dagger a_j = \delta_{jk}.$$

The Hamiltonian operator (3) may be compactly expressed as

$$H_1(t) = H_0 + \vec{\mathbf{f}}(t)\cdot\vec{\mathbf{a}} + \vec{\mathbf{f}}^*(t)\cdot\vec{\mathbf{a}}^\dagger, \tag{5}$$

with

$$H_0 = \hbar\omega(\vec{\mathbf{a}}^\dagger\cdot\vec{\mathbf{a}} + \tfrac{3}{2})$$

and

$$\vec{\mathbf{f}}(t) = -\frac{Z_1 e^2}{[R(t)]^3}\left(\frac{\hbar}{2\mu\omega}\right)^{1/2}\vec{\mathbf{R}}(t).$$

The unitary time-development operator in the Schrödinger picture corresponding to the Hamiltonian (5) and accounting for the evolution of the system from an arbitrary time $t_1$ to an arbitrary time $t_2$ can be shown to be

$$T(t_2, t_1) = e^{i\phi(t_2, t_1)}\exp(-i\omega\vec{\mathbf{a}}^\dagger\cdot\vec{\mathbf{a}}t_2) \times \exp[-i\vec{\mathbf{g}}(\omega; t_2, t_1)\cdot\vec{\mathbf{a}} - i\vec{\mathbf{g}}^*(\omega; t_2, t_1)\cdot\vec{\mathbf{a}}^\dagger] \times \exp(i\omega\vec{\mathbf{a}}^\dagger\cdot\vec{\mathbf{a}}t_1), \tag{6}$$

where

$$\vec{\mathbf{g}}(\omega; t_2, t_1) = \frac{1}{\hbar}\int_{t_1}^{t_2} e^{-i\omega s}\,\vec{\mathbf{f}}(s)\,ds \tag{7}$$

and $\phi(t_2, t_1)$ is a real phase function.

The perturbation $V_2(t)$ modifies the time development of the system. To first order in the perturbation, the state develops from $\Psi(t_1)$ to $\Psi(t_2)$ according to the formula

$$\Psi(t_2) = \left(T(t_2, t_1) - \frac{i}{\hbar}\int_{t_1}^{t_2} T(t_2, t)V_2(t)T(t, t_1)\,dt\right)\Psi(t_1) = T(t_2, t_1)\left(1 - \frac{i}{\hbar}\int_{t_1}^{t_2} T(t_1, t)V_2(t)T(t, t_1)\,dt\right)\Psi(t_1). \tag{8}$$

The expectation value of an observable $A$ in the final state is, again to first order in $V_2$,

$$\langle\Psi(t_2)|A|\Psi(t_2)\rangle = \langle\Psi(t_1)|T(t_1, t_2)AT(t_2, t_1)|\Psi(t_1)\rangle + \frac{i}{\hbar}\langle\Psi(t_1)|\left(\int_{t_1}^{t_2} T(t_1, t)V_2(t)T(t, t_1)\,dt,\ T(t_1, t_2)AT(t_2, t_1)\right)|\Psi(t_1)\rangle. \tag{9}$$

Central to the theory are thus operator transforms of the type

$$\overline{V}_2(t, t_1) = T(t_1, t)V_2(t)T(t, t_1). \tag{10}$$

Since $V_2(t)$ is a quadratic form of the operators $a_j$ and $a_j^\dagger$, it is useful to note that standard operator identities give the results

$$T(t_1, t)a_j T(t, t_1) = a_j e^{-i\omega(t-t_1)} - ig_j^*(\omega; t, t_1)e^{-i\omega t} \tag{11}$$

and the conjugate relation

$$T(t_1, t)a_j^\dagger T(t, t_1) = a_j^\dagger e^{i\omega(t-t_1)} + ig_j(\omega; t, t_1)e^{i\omega t}. \tag{12}$$

The transform of an operator which can be expressed as a polynomial of the $a_j$ and $a_j^\dagger$ is simply obtained by replacing the lowering and raising operators by their transforms.

As a first application, we see that the energy operator for the free isotropic harmonic oscillator

undergoes the transformation

$$T(t_1, t_2)H_0T(t_2, t_1) = H_0 + \hbar\omega\vec{g}(\omega; t_2, t_1)\cdot\vec{g}^*(\omega; t_2, t_1) + i\hbar\omega\vec{a}\cdot\vec{g}(\omega; t_2, t_1)e^{i\omega t_1} - i\hbar\omega\vec{a}^\dagger\cdot\vec{g}^*(\omega; t_2, t_1)e^{-i\omega t_1}. \tag{13}$$

The quadrupole perturbation operator $V_2(t)$ may be written in the form

$$V_2(t) = \sum_{j,k=1}^{3} Q_{jk}(t)(a_j^\dagger a_k^\dagger + a_j a_k + 2a_j^\dagger a_k), \tag{14}$$

where the coefficients $Q_{jk}(t)$ are the elements of a real symmetric matrix:

$$Q_{jk}(t) = Q_{kj}(t) = Q_{jk}^*(t) \tag{15}$$

with a vanishing trace:

$$\sum_j Q_{jj}(t) = 0.$$

The transform of $V_2(t)$ is then found to be

$$\overline{V}_2(t, t_1) = \sum_{j,k} Q_{jk}(t)\{a_j^\dagger a_k^\dagger e^{2i\omega(t-t_1)} + a_j a_k e^{-2i\omega(t-t_1)} + 2a_j^\dagger a_k + 2i[a_j^\dagger e^{i\omega(t-t_1)} + a_j e^{-i\omega(t-t_1)}][g_k(\omega; t, t_1)e^{i\omega t} - g_k^*(\omega; t, t_1)e^{-i\omega t}]\} + F(t, t_1)1, \tag{16}$$

where $F(t, t_1)$ is a $c$-number function, whose detailed form is not relevant.

If we wish to calculalate the energy transfer and related quantities for the over-all collision, we must choose $t_1 \to -\infty$ and $t_2 \to +\infty$ in Eq. (9). We shall also assume as an initial condition that the oscillator is in the ground state $|0\rangle$ before the collision, i.e., $\Psi(-\infty) = |0\rangle$. The expectation value of the oscillator energy is then readily obtained from Eqs. (9), (13), and (16). Only the linear terms in $\overline{V}_2$ contribute to the expectation value of the commutator, and we find

$$\langle\Psi(+\infty)|H_0|\Psi(+\infty)\rangle = \tfrac{3}{2}\hbar\omega + \hbar\omega|\vec{g}(\omega)|^2 + 2i\omega\int_{-\infty}^{+\infty}\sum_{j,k} Q_{jk}(t)[g_j(\omega)e^{i\omega t} + g_j^*(\omega)e^{-i\omega t}] \times [g_k(\omega; t, -\infty)e^{i\omega t} - g_k^*(\omega; t, -\infty)e^{-i\omega t}]dt, \tag{17}$$

where the quantity $\vec{g}(\omega)$ is defined by

$$\vec{g}(\omega) = \vec{g}(\omega; +\infty, -\infty) = \frac{1}{\hbar}\int_{-\infty}^{+\infty} e^{-i\omega s}\vec{f}(s)\,ds. \tag{18}$$

The evaluation of formula (17), based on detailed assumptions about the time dependence of the coefficients $Q_{jk}(t)$, will be given in Sec. III. Before proceeding to these calculations, it is useful to relate the expectation value (17) of the oscillator energy to the total probability of exciting the oscillator from its ground state.

The probability of finding the oscillator at $t = +\infty$ still in the ground state denoted by $|0\rangle$, if it was initially in the ground state, is given by the expectation value (9) for the operator

$$A = |0\rangle\langle 0|. \tag{19}$$

The operator transform needed is

$$T(t_1, t_2)|0\rangle\langle 0|T(t_2, t_1) = \exp[-|\vec{g}(\omega; t_2, t_1)|^2]\exp[-i\omega\vec{a}^\dagger\cdot\vec{a}t_1]\exp[-i\vec{g}^*(\omega; t_1, t_2)\cdot\vec{a}^\dagger]|0\rangle \times\langle 0|\exp[-i\vec{g}(\omega; t_2, t_1)\cdot\vec{a}]\exp[i\omega\vec{a}^\dagger\cdot\vec{a}t_1]. \tag{20}$$

Substituting Eqs. (16), (19), and (20) into Eq. (9), and noting that

$$\vec{g}(\omega; t_1, t_2) = -\vec{g}(\omega; t_2, t_1), \tag{21}$$

we arrive, after some simple but lengthy manipulations, at

$$|\langle 0|\Psi(+\infty)\rangle|^2 = e^{-|\vec{g}(\omega)|^2}\left(1 - \frac{2i}{\hbar}\int_{-\infty}^{+\infty}\sum_{jk} Q_{jk}(t)[g_j(\omega)e^{i\omega t} + g_j^*(\omega)e^{-i\omega t}][g_k(\omega; t, -\infty)e^{i\omega t} - g_k^*(\omega; t, -\infty)e^{-i\omega t}]dt + \frac{i}{\hbar}\int_{-\infty}^{+\infty}\sum_{jk} Q_{jk}(t)[g_j(\omega)g_k(\omega)e^{2i\omega t} - g_j^*(\omega)g_k^*(\omega)e^{-2i\omega t}]dt\right). \tag{22}$$

The probability of finding the oscillator at $t=+\infty$ in the eigenstate $|n_1n_2n_3\rangle$, if it was initially in the ground state, is obtained by letting $A=|n_1n_2n_3\rangle \times\langle n_1n_2n_3|$ in Eq. (9). The resulting formula is given in the Appendix.

The second term in expression (22) arises from the terms which are linear in $a$ and $a^\dagger$ in the expansion of the exponential operators in Eq. (20). The last term, which originates from the quadratic terms in the expansion of the exponentials, vanishes if

$$\sum_{jk} Q_{jk}(-t)g_j^*(\omega)g_k^*(\omega)=\sum_{jk} Q_{jk}(t)g_j(\omega)g_k(\omega)\,. \tag{23}$$

For most applications of interest, this time-reversal symmetry condition can be satisfied by an appropriate choice of coordinate axes and time scale. The physical requirements that ensure the validity of Eq. (23) will be discussed in Sec. V. If condition (23) holds, a remarkably simple relation is established between the total excitation probability and the mean energy transfer. By comparing Eqs. (22), without the last term, and (17) we obtain

$$|\langle 0|\Psi(+\infty)\rangle|^2=e^{-\Delta E_0/\hbar\omega}\left(1-\frac{\Delta E-\Delta E_0}{\hbar\omega}\right), \tag{24}$$

where $\Delta E$ is the energy transfer,

$$\Delta E=\langle\Psi(+\infty)|H_0|\Psi(+\infty)\rangle-\tfrac{3}{2}\hbar\omega \tag{25}$$

and $\Delta E_0$ is the dipole approximation to $\Delta E$,

$$\Delta E_0=\hbar\omega|\vec{\mathrm{g}}(\omega)|^2\,. \tag{26}$$

Obviously, to lowest nonvanishing order, (24) becomes

$$|\langle 0|\Psi(+\infty)\rangle|^2\approx 1-\Delta E/\hbar\omega\,, \tag{27}$$

indicating that even when the quadrupole perturbation is included to first order, only transitions to the first excited state are important. Thus, if $|\vec{\mathrm{g}}(\omega)|^2\ll 1$, the transition probability to first order in $V_2$ is simply computed from the energy transfer given by Eq. (17).

## III. STRAIGHT-LINE TRAJECTORY MOTION

We are now prepared to calculate the energy transfer to the isotropic oscillator from a charged particle moving on a prescribed orbit. For simplicity we assume that the particle moves with constant velocity $v_1$ on a straight-line trajectory at an impact parameter $b$. In conformity with Ref. 6, we choose the coordinate system such that the particle moves in the positive $y$ direction on the line $X=-b$. Hence,

$$X(t)=-b,\quad Y(t)=v_1t,\quad Z(t)=0\,, \tag{28}$$

and consequently,

$$\begin{aligned} f_1(t)&=\frac{Z_1e^2b}{[b^2+(v_1t)^2]^{3/2}}\left(\frac{\hbar}{2\mu\omega}\right)^{1/2},\\ f_2(t)&=-\frac{Z_1e^2v_1t}{[b^2+(v_1t)^2]^{3/2}}\left(\frac{\hbar}{2\mu\omega}\right)^{1/2},\\ f_3(t)&=0\,, \end{aligned} \tag{29}$$

and

$$\begin{aligned} g_1(\omega)&=Z_1e^2\frac{2\omega}{\hbar v_1^2}\left(\frac{\hbar}{2\mu\omega}\right)^{1/2}K_1\left(\frac{\omega b}{v_1}\right),\\ g_2(\omega)&=iZ_1e^2\frac{2\omega}{\hbar v_1^2}\left(\frac{\hbar}{2\mu\omega}\right)^{1/2}K_0\left(\frac{\omega b}{v_1}\right),\\ g_3(\omega)&=0\,. \end{aligned} \tag{30}$$

The functions $K_0$ and $K_1$ are modified Bessel functions. For the quadrupole interaction we obtain from Eq. (4) the following nonvanishing coefficients for expression (14):

$$\begin{aligned} Q_{11}&=-Z_1e^2\frac{\hbar}{4\mu\omega}\frac{2b^2-(v_1t)^2}{[b^2+(v_1t)^2]^{5/2}},\\ Q_{22}&=-Z_1e^2\frac{\hbar}{4\mu\omega}\frac{2(v_1t)^2-b^2}{[b^2+(v_1t)^2]^{5/2}},\\ Q_{33}&=-Z_1e^2\frac{\hbar}{4\mu\omega}\frac{-[b^2+(v_1t)^2]}{[b^2+(v_1t)^2]^{5/2}},\\ Q_{12}&=-Z_1e^2\frac{\hbar}{4\mu\omega}\frac{-3bv_1t}{[b^2+(v_1t)^2]^{5/2}}\,. \end{aligned} \tag{31}$$

Applying these results to Eq. (17), we obtain

$$\begin{aligned} \Delta E=(Z_1e^2)^2\frac{2\omega^2}{\mu v_1^4}&\left\{\left[K_0\left(\frac{\omega b}{v_1}\right)\right]^2+\left[K_1\left(\frac{\omega b}{v_1}\right)\right]^2\right\}\\ &+\frac{2(Z_1e^2)^3}{\mu^2v_1^4b^3}\left(-K_1(u)\int_{-\infty}^{+\infty}\frac{dv\cos uv}{(1+v^2)^{5/2}}[(v^2-2)F_1(u,v)-3vF_2(u,v)]\right.\\ &\left.+K_0(u)\int_{-\infty}^{+\infty}\frac{dv\sin uv}{(1+v^2)^{5/2}}[3vF_1(u,v)-(1-2v^2)F_2(u,v)]\right), \end{aligned} \tag{32}$$

where $u = \omega b/v_1$ and[6]

$$F_1(u, v) = \int_{-\infty}^{v} dy \, \frac{\sin[u(v-y)]}{(1+y^2)^{3/2}}, \qquad F_2(u, v) = \int_{-\infty}^{v} dy \, \frac{y \sin[u(v-y)]}{(1+y^2)^{3/2}}.$$

Remarkably, Eq. (32) is in exact agreement with the fully classical result.[6] From Eqs. (30) and (31) it is seen that the symmetry condition (23) is satisfied. It follows that the total excitation probability, according to equation (27), is to the same order of accuracy

$$1 - |\langle 0|\Psi(+\infty)\rangle|^2 = \Delta E/\hbar\omega . \tag{33}$$

The underlying reasons for the agreement between the quantal and classical $\Delta E$ to this order will be discussed in Sec. V.

## IV. PERTURBATION THEORY

It is instructive to rederive Eq. (32) in conventional perturbation theory, using the free oscillator (Hamiltonian $H_0$) as the unperturbed system and the interaction $V_1(t) + V_2(t)$ as the time-dependent perturbation. The calculation is worth repeating in standard perturbation theory because the method employed in Sec. II is peculiar to the isotropic oscillator and not capable of generalization to other, and more realistic, models of the atom. The customary difficulties associated with second-order perturbation theory stand in the way of performing a reliable calculation of the $Z_1^3$ term for most systems,[9] since such a term arises from the interference of first- and second-order transition amplitudes. However, for the isotropic oscillator considerable simplifications occur due to the effect of strong selection rules, and the calculation becomes manageable and transparent. One may even hope that certain features of such a model calculation survive the generalization to more complex systems, perhaps in the form of sum rules.

The perturbation calculation is most suitably carried out by the use of spherical polar coordinates and angular momentum eigenfunctions. Hence, we now phrase the same problem as before in a new form:

$$H_0 = \frac{p^2}{2\mu} + \frac{1}{2}\mu\omega^2 r^2 ,$$

$$V_1(t) = -Z_1 e^2 \frac{\boldsymbol{r}}{R^2} P_1(\hat{r}\cdot\hat{R})$$

$$= -\frac{4\pi}{3} Z_1 e^2 \frac{r}{R^2} \sum_m (-1)^m Y_1^{-m}(\hat{R}) Y_1^m(\hat{r}), \tag{34}$$

$$V_2(t) = -Z_1 e^2 \frac{r^2}{[R(t)]^3} P_2(\hat{r}\cdot\hat{R})$$

$$= -Z_1 e^2 \frac{4\pi}{5} \frac{r^2}{R^3} \sum_m (-1)^m Y_2^{-m}(\hat{R}) Y_2^m(\hat{r}). \tag{35}$$

The effective perturbation is taken to be

$$V'(t) = V_1(t) + V_2(t), \tag{36}$$

and time-dependent perturbation theory is carried out to second order. Using the quantum numbers $n$, $l$, $m$, corresponding to an unperturbed energy,

$$E_{nlm} = \hbar\omega(2n + l + \tfrac{3}{2}) \tag{37}$$

for the isotropic harmonic oscillator, the pertinent second-order transition amplitude from the oscillator ground state to a final state $n, l, \boldsymbol{m}$, is

$$c_{nlm}(+\infty) = -\frac{i}{\hbar}\int_{-\infty}^{+\infty} dt \, \langle nlm|V'(t)|000\rangle e^{i\omega_{n0}t} \, dt - \frac{1}{\hbar^2}\int_{-\infty}^{+\infty} dt \int_{-\infty}^{t} dt' \sum_{n'l'm'} \langle nlm|V'(t)|n'l'm'\rangle$$

$$\times \langle n'l'm'|V'(t')|000\rangle \exp(i\omega_{nl,\,n'l'}t + i\omega_{n'l',\,00}t'), \tag{38}$$

where

$$\hbar\omega_{nl,\,n'l'} = E_{nlm} - E_{n'l'm'} . \tag{39}$$

The selection rules for the dipole and quadruple perturbations, defined by Eqs. (34) and (35), are very simple:

$E1$ selection rules:

$\Delta l = \pm 1$ and $\Delta n = \pm\frac{1}{2} - \frac{1}{2}\Delta l$ (but $l = 0 \not\to l' = 0$ forbidden);

$E2$ selection rules:

$$\Delta l = 0, \pm 2 \text{ and } \Delta n = -\tfrac{1}{2}\Delta l \text{ or } \Delta n = \pm 1 - \tfrac{1}{2}\Delta l$$
$$(\text{but } l = 0 \not\to l' = 0 \text{ forbidden}). \tag{40}$$

In addition, the usual selection rules for the magnetic quantum number must, of course, be satisfied.

Evidently, the only states that can be reached in first order from the ground state $(nl) = (00)$ are $(nl) = (0, 1)$, by an $E1$ transition, and $(0, 2)$, by an $E2$ transition. We shall consider only those contributions to the second-order transition amplitude which lead to final states that are also accessible

by first-order transitions, because our primary interest is in calculating the cross terms between first- and second-order transitions that arise from taking the square of the absolute value of expression (38).

It may be assumed that the orbit of the charged particle lies in the $XY$ plane, so that $Z(t)=0$ for all $t$. This choice of coordinates implies that $Y_l^m(\hat{R})=0$ for $l-m=$ odd. Hence, in the dipole interaction (34) only the terms with $m=\pm 1$, and in the quadrupole interaction (35) only the terms with $m=0, \pm 2$ survive.

Usually it is a good approximation to assume that the orbit of the charged particle is symmetric with respect to a line which bisects the angle between the directions of incidence and scattering, and this line may be chosen as the $X$ axis of the coordinate system. If the reaction of the inelastic collision on the incident particle is entirely neglected, the motion satisfies the further symmetry conditions

$$X(-t)=X(t), \quad Y(-t)=-Y(t). \tag{41}$$

If these conditions hold, the Coulomb interaction between the charged particle and the electron as well as each term in the multipole expansion are seen to be invariant under the simultaneous transformation

$$t \to -t, \quad y \to -y. \tag{42}$$

Hence, for all perturbations considered here

$$V(-t)P_y = P_y V(t) \tag{43}$$

if $P_y$ is the unitary and Hermitian operator which effects a reflection of the electron coordinates in the $xz$ plane. It is easy to see[10] that in its effect on orbital-angular-momentum eigenstates $P_y$ may be chosen to act just like the time-reversal operator $\Theta$:

$$P_y|lm\rangle = e^{i\delta}(-1)^m|l,-m\rangle = \Theta|lm\rangle, \tag{44}$$

where the real phase $\delta$ may depend on $l$, but not on $m$. From Eqs. (43) and (44) and from the antiunitarity of $\Theta$, it follows that

$$\begin{aligned}\langle n'l'm'|V(-t)|nlm\rangle &= \langle n'l'm'|V(-t)P_y^2|nlm\rangle \\ &= \langle n'l'm'|P_y V(t) P_y|nlm\rangle \\ &= \langle n'l'm'|\Theta^{-1}V(t)\Theta|nlm\rangle^* \\ &= \langle n'l'm'|V(t)|nlm\rangle^*. \end{aligned} \tag{45}$$

The time-reversal symmetry condition, $\Theta^{-1}V(t)\Theta = V(t)$, has been used in the last step of Eq. (45).

This symmetry relation has important consequences for the reality properties of the various terms in the perturbation expansion (38). It obviously follows from (45) that the first-order term in Eq. (38) must always be imaginary.

For the second-order term we can infer from condition (45) only that

$$\begin{aligned}&\mathrm{Im}\int_{-\infty}^{+\infty} dt \int_{-\infty}^{t} dt' \sum_{n'l'm'} \langle nlm|V'(t)|n'l'm'\rangle\langle n'l'm'|V'(t')|000\rangle \exp(i\omega_{nl,n'l'}t + i\omega_{n'l',00}t'), \\ &\quad = -\mathrm{Im}\int_{-\infty}^{+\infty} dt \int_{-\infty}^{t} dt' \sum_{n'l'm'} \langle nlm|V'(t')|n'l'm'\rangle\langle n'l'm'|V'(t)|000\rangle \exp(i\omega_{nl,n'l'}t' + i\omega_{n'l',00}t),\end{aligned} \tag{46}$$

with $t$ and $t'$ interchanged in the integrand. This relation can be used to show that the second-order transition amplitudes leading to the second excited state and mediated by two successive $E1$ transitions are real quantities and hence, in the evaluation of transition probabilities, cannot give rise to contributions to cross terms with the imaginary $E2$ transition amplitudes.

Taking all applicable selection rules into account, the only relevant second-order matrix elements are then

$$[\langle 01\pm 1|V_1(t)|01\pm 1\rangle\langle 01\pm 1|V_1(t')|000\rangle + \langle 01\pm 1|V_2(t)|01\mp 1\rangle\langle 01\mp 1|V_1(t')|000\rangle]\, e^{i\omega t'} \tag{47}$$

and

$$[\langle 01\pm 1|V_1(t)|02\pm 2\rangle\langle 02\pm 2|V_2(t')|000\rangle + \langle 01\pm 1|V_1(t)|020\rangle\langle 020|V_2(t')|000\rangle]\, e^{-i\omega t + 2i\omega t'}. \tag{48}$$

The transition amplitudes (47) and (48) can be illustrated diagrammatically in Fig. 1.

The evaluation of the needed matrix elements between the eigenstates of the isotropic harmonic oscillator is straightforward and gives the result:

$$\langle 01\pm 1|V_1(t)|000\rangle = Z_1 e^2 \left(\frac{\hbar}{\mu\omega}\right)^{1/2} \frac{\pm X(t) - iY(t)}{2[R(t)]^3}, \tag{49}$$

$$\langle 01\pm 1|V_1(t)|02\pm 2\rangle = Z_1 e^2 \left(\frac{\hbar}{\mu\omega}\right)^{1/2} \frac{\pm X(t) + iY(t)}{\sqrt{2}[R(t)]^3}, \tag{50}$$

$$\langle 01\pm1|V_1(t)|020\rangle = Z_1e^2\left(\frac{\hbar}{\mu\omega}\right)^{1/2}\frac{\mp X(t)+iY(t)}{\sqrt{12}[R(t)]^3}, \tag{51}$$

$$\langle 01\pm1|V_2(t)|01\pm1\rangle = Z_1e^2\left(\frac{\hbar}{\mu\omega}\right)\frac{-[X(t)]^2-[Y(t)]^2}{4[R(t)]^5}, \tag{52}$$

$$\langle 01\pm1|V_2(t)|01\mp1\rangle = Z_1e^2\,\frac{\hbar}{\mu\omega}\,\frac{3[X(t)\mp iY(t)]^2}{4[R(t)]^3}, \tag{53}$$

$$\langle 02\pm2|V_2(t)|000\rangle = -Z_1e^2\,\frac{\hbar}{\mu\omega}\,\frac{3}{4\sqrt{2}}\,\frac{[X(t)\mp iY(t)]^2}{[R(t)]^5}, \tag{54}$$

$$\langle 020|V_2(t)|000\rangle = Z_1e^2\,\frac{\hbar}{\mu\omega}\,\frac{\sqrt{3}}{4}\,\frac{[X(t)]^2+[Y(t)]^2}{R^5}. \tag{55}$$

If the calculation is now specialized to a straight-line trajectory motion for the charged particle, as assumed in Sec. III, the transition probability can be evaluated by choosing the representation (28) for $X(t)$ and $Y(t)$ and working out the transition probability to order $(Z_1e)^3$ from Eq. (38) with the use of (47) and (48), and with the matrix elements (49)–(55). The first-order $E1$ transition amplitude becomes, as usual,

$$-\frac{i}{\hbar}\int_{-\infty}^{+\infty}\langle 01\pm1|V_1(t)|000\rangle e^{i\omega t}\,dt = \frac{Z_1e^2i}{2(\hbar\mu\omega)^{1/2}}\int_{-\infty}^{+\infty}\frac{\pm b+iv_1t}{[R(t)]^3}e^{i\omega t}\,dt$$
$$= -iZ_1e^2\left(\frac{\omega}{\hbar\mu}\right)^{1/2}\frac{1}{v_1^2}\left[K_0\left(\frac{\omega b}{v_1}\right)\mp K_1\left(\frac{\omega b}{v_1}\right)\right]. \tag{56}$$

The cross terms arising from the product of this expression with the much more complicated second-order amplitudes may be combined and transformed by some straightforward but lengthy algebra. In agreement with Eqs. (32) and (33), the final transition probability up to order $(Z_1e)^3$ is

$$\sum_m |c_{01m}(+\infty)|^2 = (Z_1e^2)^2\,\frac{2\omega}{\hbar\mu v_1^4}\{[K_0(u)]^2+[K_1(u)]^2\} + (Z_1e^2)^3\,\frac{2}{\hbar\omega(\mu v_1^2)^2b^3}$$
$$\times\left(-K_1(u)\int_{-\infty}^{+\infty}\frac{dv\cos uv}{(1+v^2)^{5/2}}[(v^2-2)F_1(u,v)-3vF_2(u,v)]\right.$$
$$\left.+K_0(u)\int_{-\infty}^{+\infty}\frac{dv\sin uv}{(1+v^2)^{5/2}}[3vF_1(u,v)-(1-2v^2)F_2(u,v)]\right), \tag{57}$$

where $u=\omega b/v_1$.

The quadrupole interaction causes transitions from the ground state of the isotropic harmonic oscillator to the states $(02\pm2)$ and $(020)$, permitted by the selection rules (40). It may be useful to record the first-order $E2$ transition amplitudes to these states:

$$-\frac{i}{\hbar}\int_{-\infty}^{+\infty}\langle 02\pm2|V_2(t)|000\rangle e^{2i\omega t}\,dt = iZ_1e^2\,\frac{2\sqrt{2}\omega}{\mu v_1^3}\left[K_1'\left(\frac{2\omega b}{v_1}\right)\pm K_1\left(\frac{2\omega b}{v_1}\right)\right] \tag{58}$$

and

$$-\frac{i}{\hbar}\int_{-\infty}^{+\infty}\langle 020|V_2(t)|000\rangle e^{2i\omega t}\,dt = -iZ_1e^2\,\frac{\sqrt{3}}{b\mu v_1^2}K_1\left(\frac{2\omega b}{v_1}\right). \tag{59}$$

Owing to the proportionality of the linear dimensions of the oscillator to $\sqrt{\hbar}$, the quadrupole transition amplitude is independent of Planck's constant.

## V. DISCUSSION

The analysis of "distant" collisions between a charged particle and an "atom" (i.e., isotropic harmonic oscillator), carried through in the previous sections, relies on a double expansion. The multipole expansion of the electrostatic potential and the perturbation expansion of the transition amplitude together produce a hierarchy of higher-order terms whose relative magnitudes must be assessed with care. If the selection rules (40) are taken into account but time-reversal symmetry conditions disregarded, leading contributions to the terms of order $Z_1^3$ in the transition probability may be expected to arise from the interference of (1) a first-order quadrupole transition with a

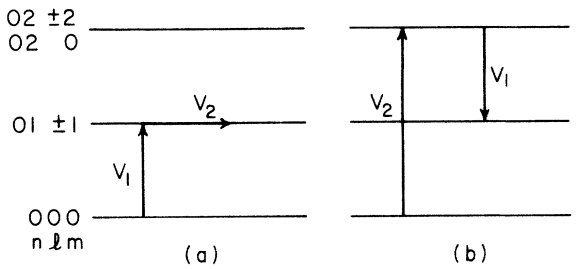


FIG. 1. Diagram representation of the effective second-order electric dipole and quadrupole transitions from the ground state of the isotropic harmonic oscillator.

second-order double dipole transition, and (2) a first-order dipole transition with a second-order dipole-quadrupole or quadrupole-dipole transition. Evidently, as was shown in Sec. IV, if the motion of the particle is assumed to be unaffected by the interaction with the electron, time-reversal symmetry eliminates case (1) and permits only contributions from case (2), as depicted in Fig. 1. The time-reversal symmetry conditions,

$$V(-t)P_y = P_y V(t) \quad \text{and} \quad \Theta^{-1} V(t) \Theta = V(t), \tag{60}$$

of Sec. IV may be easily shown to imply the symmetry condition (23) of Sec. II. Applied to the dipole interaction,

$$V_1(t) = \vec{f}(t) \cdot \vec{a} + \vec{f}^*(t) \cdot \vec{a}^\dagger, \tag{61}$$

the conditions (60) show that $\vec{f}(t)$ must be real, and

$$f_1(-t) = f_1(t), \quad f_2(-t) = -f_2(t), \quad f_3(-t) = f_3(t). \tag{62}$$

Similarly, applied to Eqs. (14) and (15), the time-reversal symmetry conditions require that

$$Q_{12}(-t) = -Q_{12}(t), \quad Q_{23}(-t) = -Q_{23}(t), \quad Q_{31}(-t) = Q_{31}(t),$$
$$Q_{ii}(-t) = Q_{ii}(t) \quad (i = 1, 2, 3). \tag{63}$$

All of these properties of $\vec{f}(t)$ and $Q_{ij}(t)$ taken together ensure that relation (23) is satisfied. It is thus quite understandable that, up to terms of order $Z_1^3$, the energy transfer may be calculated from the transition probability to the first excited state only:

$$\Delta E = \hbar\omega(1 - |\langle 0|\Psi(+\infty)\rangle|^2). \tag{64}$$

Such a simple relation cannot be expected to hold if the calculation is carried to higher order, or if the incident particle is appreciably decelerated by the inelastic collision.

The integrals appearing in Eq. (32) have been evaluated numerically.[11] The over-all role of the "distant" collisions can be estimated from the excitation probability for impact parameter $b$ by integrating from a minimum impact parameter $a$ to infinity, thereby defining a total excitation cross section for distant collisions:

$$\sigma_d = 2\pi \int_a^\infty (1 - |\langle 0|\Psi(+\infty)\rangle|^2) b\, db. \tag{65}$$

If relation (64) holds, this cross section can be expressed in terms of the contribution of the distant collisions to the stopping power:

$$-\left(\frac{dE}{dx}\right)_d = 2\pi n \int_a^\infty \Delta E b\, db = n\hbar\omega\sigma_d, \tag{66}$$

where $n$ is the number of target atoms per unit volume.

Since at high impact velocities, transition probabilities, cross sections, and energy losses depend on the parameter $\xi = a\omega/v_1$ only logarithmically, when $\xi \ll 1$, the choice of the minimum impact parameter does not affect the results of the calculations strongly. At such high velocities, it appears reasonable to suppose that the close collisions, with impact parameter less than $a$, make comparatively small contributions to the $Z_1^3$ correction term. Such a behavior is said to be expected, since, at high velocities, close collisions may be regarded as impulsive binary collisions between the incident particle and the atomic electron, whose binding to the nucleus is neglected. The strict $Z_1^2$ proportionality of the Rutherford scattering cross section, appropriate to such a "binary encounter," is then invoked to suggest that close collisions make negligible contributions to the $Z_1^3$ corrections.[6]

It is not clear that at all but the very highest impact velocities the close collisions can be safely ignored. Thus, for instance, Bloch's version of the stopping power formula,[12]

$$-\frac{dE}{dx} = n\frac{4\pi Z_1^2 e^4}{\mu v_1^2}\left[\ln\frac{2\mu v^2}{I} + \psi(1) - \mathrm{Re}\psi\left(1 + i\frac{Z_1 e^2}{\hbar v_1}\right)\right] \tag{67}$$

contains in the last term corrections to the $Z_1^2$ law, which are important if $Z_1 e^2/\hbar v_1$ is not very small. However, it should be noted that these corrections, when expanded in powers of $Z_1$, give rise only to even powers, and no $Z_1^3$ term appears. (In the early, fully classical, theory of energy loss,[13] the delicate process of joining together the distant and close collision regimes also led to a more complicated $Z_1$ dependence, although the close collisions were treated as pure Rutherford scattering.)

Since the unimportance of close collisions cannot be taken for granted, it would be desirable to have available the results of a second-order perturbation calculation—either in a semiclassical or Born approximation—using the full Coulomb interaction between incident particle and atomic elec-

tron, at least for close collisions with large momentum transfer. The usual difficulties with the summation over intermediate states have precluded reliable calculations of this kind except for very special cases, and then only with the use of additional approximations whose accuracy is difficult to establish.[9]

Leaving the close collisions aside the present semiclassical calculation, like its classical predecessor,[6] shows the details of a full second-order perturbation calculation for the distant collisions with an oscillator model of the atom. The relation between the semiclassical and the entirely classical theory is best analyzed by considering the equations of motion in the Heisenberg picture, rather than the Schrödinger picture, which was used in Secs. II–IV.

The Hamiltonian

$$H=\hbar\omega(\vec{a}^{\dagger}\cdot\vec{a}+\tfrac{3}{2})+\vec{f}(t)\cdot\vec{a}+\vec{f}^{*}(t)\cdot\vec{a}^{\dagger}+\sum_{j,k=1}^{3}Q_{jk}(t)(a_j^{\dagger}a_k^{\dagger}+a_ja_k+2a_j^{\dagger}a_k) \tag{68}$$

gives the equation of motion:

$$i\hbar\frac{da_k(t)}{dt}=[a_k(t),H]=\hbar\omega a_k(t)+f_k^{*}(t)+2\sum_{l=1}^{3}Q_{kl}(t)[a_l(t)+a_l^{\dagger}(t)]. \tag{69}$$

Using the definition (7), this can also be written as an integral equation:

$$a_k(t)e^{i\omega t}=a_k-ig_k^{*}(\omega;t,-\infty)-\frac{2i}{\hbar}\sum_l\int_{-\infty}^{t}e^{i\omega t'}Q_{kl}(t')[a_l(t')+a_l^{\dagger}(t')]dt' \tag{70}$$

where $a_k=\lim a_k(t)e^{i\omega t}$ as $t\to-\infty$. If the quadrupole perturbation is small, this equation may be solved by iteration. The solution, correct to first order in $Q$, is

$$a_k(t)e^{i\omega t}=a_k-ig_k^{*}(\omega;t,-\infty)-\frac{2i}{\hbar}\sum_l\int_{-\infty}^{t}Q_{kl}(t')e^{i\omega t'}[a_le^{-i\omega t'}+a_l^{\dagger}e^{i\omega t'}$$
$$+ig_l(\omega;t',-\infty)e^{i\omega t'}-ig_l^{*}(\omega;t,-\infty)e^{-i\omega t'}]dt'. \tag{71}$$

Since the operators $a_k(t)$ and $a_k^{\dagger}(t)$ are linearly related to their initial values, $a_k$ and $a_k^{\dagger}$, the expectation values of the lowering and raising operators, as well as of the Cartesian dynamical variables $x_k$ and $p_k$, which are linear combinations of the $a_k$ and $a_k^{\dagger}$, must agree with the solutions of the classical equations of motion. When expectation values of quadratic forms of $a$ and $a^{\dagger}$ operators are calculated, the classical and quantal results generally differ.[14] The energy transfer is the expectation value of the operator,

$$H_0(t)-H_0(-\infty)=\hbar\omega[\vec{a}^{\dagger}(t)\cdot\vec{a}(t)-\vec{a}^{\dagger}\cdot\vec{a}]. \tag{72}$$

When expression (71) is substituted into (72), to first order in $Q$ only quadratic terms of the form $a_k^{\dagger}a_l^{\dagger}$ and $a_k\,a_l$ occur. Hence, the expectation value of (72) in the ground state of the oscillator must be the same as the classical energy transfer to an oscillator, initially at rest, evaluated to first order in the quadrupole, and arbitrarily high order in the dipole, interaction. Quantum corrections are expected when the calculation is carried to second order in $Q$.

The relative importance of higher perturbations can be judged by noting that the $E1$ interaction is approximately measured by the strength parameter

$$\frac{Z_1e^2}{\hbar v_1}\left(\frac{\hbar}{\mu\omega}\right)^{1/2}\frac{1}{a},$$

whereas the $E2$ interaction has the strength

$$\frac{Z_1e^2}{\hbar v_1}\frac{\hbar}{\mu\omega}\frac{1}{a^2}.$$

It is evident that the multipole expansion converges rapidly only if $a$ is substantially larger than the linear dimensions of the atom.

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## APPENDIX

The excitation probability from the ground state of the oscillator to the state $|n_1n_2n_3\rangle$ has been

worked out by methods described in Sec. II. If $n_1$, $n_2$, $n_3$ are the Cartesian quantum numbers, corresponding to an energy spectrum

$$E = \hbar\omega(n_1 + n_2 + n_3 + \tfrac{3}{2})$$

the excitation probability from the initial state $|000\rangle$ is, in analogy with Eq. (22), given by

$$|\langle n_1 n_2 n_3|\Psi(+\infty)\rangle|^2 = e^{-|\tilde{g}(\omega)|^2}\Bigg[\prod_{l=1}^{3}\frac{|g_l(\omega)|^{2n_l}}{n_l!} + \frac{i}{\hbar}\int_{-\infty}^{\infty}dt\sum_{j,k=1}^{3}Q_{jk}[e^{i\omega t}g_j(\omega)g_k(\omega) - e^{-2i\omega t}g_j^*(\omega)g_k^*(\omega)]$$
$$\times\Bigg(\prod_{l=1}^{3}\frac{|g_l(\omega)|^{2n_l}}{n_l!} - 2\prod_{l=1}^{3}\frac{|g_l(\omega)|^{2(n_l-\delta_{jl})}}{(n_l-\delta_{jl})!} + \prod_{l=1}^{3}\frac{|g_l(\omega)|^{2(n_l-\delta_{jl}-\delta_{kl})}}{(n_l-\delta_{jl}-\delta_{kl})!}\Bigg)$$
$$-\frac{2i}{\hbar}\int_{-\infty}^{\infty}dt\sum_{j,k}Q_{jk}[g_j(\omega)e^{i\omega t} + g_j^*(\omega)e^{-i\omega t}][g_k(\omega;t,-\infty)e^{i\omega t} - g_k^*(\omega;t,-\infty)e^{-i\omega t}]$$
$$\times\Bigg(\prod_{l=1}^{3}\frac{|g_l(\omega)|^{2n_l}}{n_l!} - \prod_{l=1}^{3}\frac{|g_l(\omega)|^{2(n_l-\delta_{jl})}}{(n_l-\delta_{jl})!}\Bigg)\Bigg],$$

where it is understood that terms having denominators such as $(n_l - \delta_{jl})!$ are zero if $(n_l - \delta_{jl})$ is a negative integer.

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