## Time-Dependent Perturbation Theory: The Photoelectric Effect

- This handout mirrors the treatment of the photoelectric effect on Shankar pp. 499–506, with two principal differences: (1) The perturbing Hamiltonian is written $H_{1E} = e\boldsymbol{E}\cdot\boldsymbol{R}$ instead of $H_{1A} = (e/mc)\boldsymbol{A}\cdot\boldsymbol{P}$. (2) The system is assumed to occupy a cubic box of sides $L$, whereas Shankar treats an infinite system. We comment on the significance of these differences at the end.

- The initial state is taken to belong to the innermost (or $K$) shell of a hydrogen-like atom of effective nuclear charge $Ze$, with wave function $\langle \boldsymbol{r}|i\rangle = \pi^{-1/2}(Z/a_0)^{3/2}\exp(-Z|\boldsymbol{r}|/a_0)$, where $a_0 = \hbar^2/me^2$ is the Bohr radius. This state has energy $\varepsilon_i = -Z^2e^2/2a_0 = -(Z\alpha)^2mc^2/2$, $\alpha = e^2/\hbar c$ being the fine-structure constant. The characteristic size of the orbital is $r_0 = a_0/Z = \hbar/(Z\alpha mc)$.

  We consider a monochromatic electromagnetic plane wave, $\boldsymbol{E}(\boldsymbol{r},t) = \boldsymbol{E}_0\cos(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)$. The electric dipole approximation is valid provided that $|\boldsymbol{k}|r_0 \ll 1$, or equivalently, $\hbar\omega \ll (Z\alpha)mc^2$. We will consider frequencies in the window $(Z\alpha)^2mc^2 \ll \hbar\omega \ll (Z\alpha)mc^2$, where not only can we make the dipole approximation, but the final-state energy is sufficiently high that the final state should be well-described by a plane wave of the form $\langle\boldsymbol{r}|f\rangle = L^{-3/2}\exp(i\boldsymbol{p}_f\cdot\boldsymbol{r}/\hbar)$ having an energy $\varepsilon_f = |\boldsymbol{p}_f|^2/2m$. (See Shankar p. 500 and the end of this handout for discussion of this plane-wave approximation.)

- In the dipole approximation, we need to calculate the dipole matrix element

$$\begin{aligned}\boldsymbol{r}_{fi} &= \langle f|\boldsymbol{R}|i\rangle = A\int d^3\boldsymbol{r}\; e^{-i\boldsymbol{p}_f\cdot\boldsymbol{r}/\hbar}\;\boldsymbol{r}\; e^{-Z|\boldsymbol{r}|/a_0} \\ &= A\times i\hbar\,\frac{\partial}{\partial\boldsymbol{p}_f}\int d^3\boldsymbol{r}\; e^{-i\boldsymbol{p}_f\cdot\boldsymbol{r}/\hbar}\; e^{-Z|\boldsymbol{r}|/a_0} = i\hbar\,\frac{\partial}{\partial\boldsymbol{p}_f}\langle f|i\rangle,\end{aligned}$$

  where $A = \pi^{-1/2}(Z/La_0)^{3/2}$.

  The overlap integral is straightforward to evaluate (see Shankar p. 504):

$$\langle f|i\rangle = A\int d^3\boldsymbol{r}\; e^{-i\boldsymbol{p}_f\cdot\boldsymbol{r}/\hbar}e^{-Z|\boldsymbol{r}|/a_0} = \frac{8\pi AZ/a_0}{[(Z/a_0)^2+(p_f/\hbar)^2]^2}.$$

  Therefore

$$\boldsymbol{r}_{fi} = i\hbar\;\frac{8\pi AZ/a_0}{[(Z/a_0)^2+(p_f/\hbar)^2]^3}\left(\frac{-4\boldsymbol{p}_f}{\hbar^2}\right).$$

  Noting that $(Z/a_0)^2+(p_f/\hbar)^2 = 2m(\varepsilon_f-\varepsilon_i)/\hbar^2$, we find

$$\boldsymbol{r}_{fi} = -\frac{2i\hbar}{m(\varepsilon_f-\varepsilon_i)}\;\boldsymbol{p}_f\langle f|i\rangle = -i\;\frac{4\pi AZ\hbar^5}{a_0m^3(\varepsilon_f-\varepsilon_i)^3}\;\boldsymbol{p}_f. \tag{1}$$

- Fermi's Golden Rule gives the scattering rate from $|i\rangle$ to $|f\rangle$ as

$$R_{i\to f} = \frac{2\pi}{\hbar}\left|\frac{e}{2}\,\boldsymbol{E}_0\cdot\boldsymbol{r}_{fi}\right|^2\delta(\varepsilon_f-\varepsilon_i-\hbar\omega).$$

In order to calculate the differential scattering cross-section $d\sigma/d\Omega$, defined by

$$\frac{d\sigma}{d\Omega} = \frac{\text{power absorbed by atom while emitting electrons into solid angle } d\Omega}{(\text{incident energy flux of electromagnetic field}) \times d\Omega},$$

we need to find the density of final states $\boldsymbol{p}_f$. If we apply periodic boundary conditions to the cubic box, then the allowed final states obey

$$(p_f)_j = \hbar\,\frac{2\pi n_j}{L} = \frac{h n_j}{L} \qquad \text{for } j = x, y, z.$$

Thus, the number of allowed states in a momentum-space volume element $p_f^2\, dp_f\, d\Omega$ is

$$\left(\frac{L}{h}\right)^3 p_f^2\, dp_f\, d\Omega = \left(\frac{L}{h}\right)^3 m p_f\, d\varepsilon_f\, d\Omega,$$

and the power absorbed by the atom in scattering into solid angle $d\Omega$ is

$$P_{i\to d\Omega} = \hbar\omega R_{i\to d\Omega} = \hbar\omega d\Omega \int d\varepsilon_f \left(\frac{L}{h}\right)^3 m p_f\, R_{i\to f} = \frac{e^2\hbar p_f^3 E_0^2}{\pi}\left(\frac{Z}{m\omega a_0}\right)^5 \left|\hat{\boldsymbol{E}}_0\cdot\hat{\boldsymbol{p}}_f\right|^2 d\Omega.$$

The incident energy flux of the electromagnetic wave is $J_{\text{in}} = uc = (c/4\pi)\,|\boldsymbol{E}(\boldsymbol{r},t)|^2$, or, averaged over one complete cycle, $J_{\text{in}} = (c/8\pi)\,|\boldsymbol{E}_0|^2$. Thus,

$$\frac{d\sigma}{d\Omega} = \frac{P_{i\to d\Omega}}{J_{\text{in}} d\Omega} = \frac{8e^2\hbar p_f^3}{c}\left(\frac{Z}{m\omega a_0}\right)^5 \left|\hat{\boldsymbol{E}}_0\cdot\hat{\boldsymbol{p}}_f\right|^2. \tag{2}$$

- **Comment 1**: The finite system size does not enter the final result. If one works with an infinite system, the correct density of final states is ensured through the delta-function normalization of the plane wave, i.e., $\langle \boldsymbol{r}|\boldsymbol{p}\rangle = (2\pi\hbar)^{-3/2}\exp(i\boldsymbol{p}\cdot\boldsymbol{r}/\hbar)$.

- **Comment 2**: Equation (2) agrees, for instance, with that obtained from $H_{1E}$ in *Quantum Theory of Light* by R. Loudon (Clarendon Press, Oxford, 1973). On the other hand, this $d\sigma/d\Omega$ is 4 times greater than that given by Shankar, Merzbacher, and Sakurai, all of whom use $H_{1A}$.

  This discrepancy appears to stem from the fact that the general result

  $$\langle f|\boldsymbol{P}|i\rangle = \langle f|m\, d\boldsymbol{R}/dt|i\rangle = \frac{im}{\hbar}\langle f|[H,\boldsymbol{R}]|i\rangle = \frac{im(\varepsilon_f - \varepsilon_i)}{\hbar}\langle f|\boldsymbol{R}|i\rangle$$

  holds only if $i\rangle$ and $|f\rangle$ are *exact* eigenstates of the same Hamiltonian. Here, $|f\rangle$ is only an approximate version of the true final state, which is a plane wave plus an incoming spherical wave (see Merzbacher p. 502). Since $|f\rangle$ is not a true eigenstate of the Coulomb Hamiltonian, different formulations of the dipole approximation are not guaranteed to produce the same result. It turns out that $\boldsymbol{r}_{fi}$ given in Eq. (1) is twice the correct value. It can be shown [e.g., see Ch. 12 of *Intermediate Quantum Mechanics* by H. A. Bethe and R. Jackiw (2nd Edition, W. A. Benjamin, Reading, Massachussets, 1968)] that using $H_{1E}$ with the exact final state wave functions yields the result obtained using $H_{1A}$ with the plane-wave approximate wave functions.

  The $H_{1A}$ formulation does not always yield superior results. It is the $H_{1E}$ version that gives the correct frequency distribution for photons emitted from finite-lifetime excited states [W. E. Lamb, Jr., Phys. Rev. **85**, 259 (1952).]

  These examples show that calculating the effects of radiation on matter is very subtle!