of fields. Therefore, SLATER and KIRKWOOD (loc. cit.) have substituted the HARTREE eigenfunction \( u_0 \). In addition they improved the form of the function \( \varphi \) by setting

\[
\varphi = \alpha r_1^\alpha r_2^\beta (z_1 + z_2),
\]

in which the two parameters \( \alpha \) and \( \beta \) are disposable. The minimum corresponds to a \( \nu \) of about \( \frac{1}{2} \); this means that the eigenfunction is more strongly perturbed by the electric field when the electrons are far from the nucleus than when they are near the nucleus. This makes good sense. The calculation yields

\[
E_2 = -0.715.
\]

From this the dielectric constant is evaluated from (58.3) with the result

\[
\varepsilon = 1.0000715,
\]

whereas the observed value is

\[
\varepsilon = 1.000074.
\]

The agreement is satisfactory.

IV. Interaction with radiation.

a) Discrete spectrum.

59. General formulas. \( \alpha \) The dipole approximation. We start from the fundamental formula of radiation theory for the probability of a spontaneous transition of an atom from \( n \) to a state \( n' \) (energies \( E_n \) and \( E_{n'} \)), with the emission of one photon. Let \( \mathbf{k} \) be the propagation vector, \( \mathbf{k} = |\mathbf{k}| \) the wave number, \( \nu_{n,n'} \) and \( \omega_{n,n'} \) the "ordinary" and "angular" frequency of the photon. We then have the BOHR energy relation

\[
\omega_{n,n'} = 2\pi \nu_{n,n'} = c k = \frac{1}{\hbar} (E_n - E_{n'}). \tag{59.1}
\]

If the photon has polarization direction \( x \) and a propagation vector \( \mathbf{k} \) in the solid angle \( d\Omega \), the fundamental transition probability per unit time is

\[
W_{n,n'}(k, \mathbf{x}) d\Omega = \frac{\varepsilon^2 \hbar \omega_{n,n'}}{2\pi m c^2} |D_{n,n'}^{x}|^2 d\Omega. \tag{59.2}
\]

In (59.2), \( D \) is the following matrix element

\[
D_{n,n'}^{x} = \int u_{n, x}^* \sum_i e^{i \mathbf{k} \cdot \mathbf{r}_i} \frac{\partial u_n}{\partial x_i} d\tau \tag{59.3}
\]

where \( \mathbf{r}_i \) is the position of the \( i \)-th atomic electron and the integral extends over the configuration space of all the electrons.

The fundamental expression (59.2), (59.3) is derived elsewhere from quantum electrodynamics. Crudely speaking, the matrix element (59.3) is similar to that

\[1\] More correctly, they have used an analytic function derived by SLATER, which agrees very closely with the HARTREE eigenfunction.

\[2\] Here \( n \) denotes all the quantum numbers which specify the state, not merely the principal quantum number.

\[3\] \( \hbar \) is the "rationalized" PLANCK'S constant \( \hbar/2\pi \).

\[4\] We shall mainly discuss \( W_{n,n'} \), the probability for the spontaneous emission of a photon. Two other related quantities are the probabilities for absorption of a photon (transition of the atom from a lower to a higher state) and for the emission of a photon, which is induced by the exposure of the atom to radiation. These probabilities can be obtained from \( W_{n,n'} \) by the so-called EINSTEIN relations discussed in ref. [5], Chap. 4, Sect. 1 (see also our Sect. 69).

\[5\] See for instance, ref. [2], [5] and [6].

H. A. Bethe et al., Quantum Mechanics of One- and Two-Electron Atoms

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which one would obtain from (45.2) by putting $A$ equal to the vector potential of a classical electromagnetic wave with polarization direction $x$ and propagation vector $k$. We merely list the approximations made in deriving (59.2), (59.3) from quantum electrodynamics. (1) The electrons have been treated nonrelativistically and the Schrödinger equation has been used instead of the Dirac or Pauli equations (neglect of magnetic moment and of specific relativistic effects). (2) The interaction of the electron with the radiation field has been treated as a small perturbation (with the fine structure constant $\alpha$ as the perturbation parameter) and only the lowest order term kept in the expansion in powers of $\alpha$. We are thus neglecting processes involving the simultaneous emission or absorption of two or more photons (and also small radiative corrections akin to the Lamb shift).

In most cases one can simplify (59.3) considerably by making a further approximation: The important distances $r_i$ of the electrons from the nucleus are of the order of the Bohr radius of the atom, i.e. about $10^{-8}$ cm for low nuclear charge $Z$. For transitions in the discrete spectrum for low $Z$ the wave number $k = 2\pi/\lambda$ of the emitted light is much smaller than $10^8$ cm$^{-1}$, e.g. for visible light $k$ is of order $10^6$ cm$^{-1}$. The exponent $k \cdot r_i$ in the exponential in (59.3) is thus small and we can replace the exponential by unity$^1$, i.e. we "neglect retardation" and use the "electric dipole approximation". In this approximation $D_{n' n}$ is the $x$-component of a vector $D_{n' n}$ which does not depend on $k$,

$$D_{n' n} = \int u_{n'}^* \sum_i \nabla_i u_n \, d\tau.$$  

(59.4)

The vector $D_{n' n}$ is simply $i/\hbar$ times the matrix element $p_{n' n}$, for the transition $n \rightarrow n'$, of the total linear momentum operator $p = \sum p_i = -i\hbar \sum \nabla_i$. It is often useful to write $D_{n' n}$ in a different form (to be proved in Sect. 59B),

$$D_{n' n} = \frac{i}{\hbar} p_{n' n} = \frac{i m}{\hbar} v_{n' n} = \frac{m}{\hbar} \omega_{n' n} r_{n' n}.$$ \hspace{1cm} (59.5)

In (59.5), $v$ and $r$ are the sum of electron velocities and positions, respectively, $\omega_{n' n}$ is given$^2$ by (59.1) and $r_{n' n}$ is the dipole matrix element

$$r_{n' n} = \int u_{n'}^* \sum_i r_i u_n \, d\tau.$$ \hspace{1cm} (59.6)

Substituting (59.5) into (59.2), we obtain:

$$W(\Omega, j) \, d\Omega = \frac{\sigma^2}{2\pi \hbar c^5} \omega_{n' n}^3 (e_j \cdot r_{n' n})^2 \, d\Omega.$$ \hspace{1cm} (59.7)

(59.7) is the probability that an atom will undergo a transition from the state $n$ to $n'$ and emit light of polarization direction $e_j$ into the solid angle $d\Omega$. The intensity of the light emitted into the solid angle $d\Omega$ in erg/sec is obtained by multiplying the probability by the energy of the light quantum $h \nu = \hbar \omega$:

$$J_j d\Omega = \frac{\sigma^2}{2\pi c^4} \omega^4 (e_j \cdot r_{n' n})^2 \, d\Omega.$$ \hspace{1cm} (59.8)

The above is precisely the classical formula for the intensity of light emitted by an oscillating dipole having dipole moment $e r_{n' n} e_i n' e_f$ and frequency $\nu_{n' n}$. For

$^1$ The order of magnitude of $kr_i$ increases with $Z$ and for very large $Z$ this approximation is no longer very good. The approximation also fails, even for small $Z$, for transitions to states in the continuum of very high energy (Sects. 72 and 73). See also Sect. 66 for the effect of higher terms in the expansion of the exponential in powers of $kr_i$.

$^2$ Note that the last form of (59.5) shows that the transition probability between states of equal energy is zero ($\omega_{n' n'}$, i.e. the photon frequency, is zero).