In turn we can now calculate the eigenvector correction $\Psi_n^{(2)}$. Applying the same method as before to (17.37), we find

$$\Psi_n^{(2)} = C_n^{(2)}\Psi_n^{(0)} - \frac{1 - P_n^{(0)}}{E_n^{(0)} - H_0}(E_n^{(1)} - V)\Psi_n^{(1)}$$

Again we may set $C_n^{(2)} = 0$, i.e., $P_n^{(0)}\Psi_n^{(2)} = 0$. Substituting also (17.35) for $\Psi_n^{(1)}$, we obtain

$$\Psi_n^{(2)} = -\frac{1 - P_n^{(0)}}{E_n^{(0)} - H_0}(E_n^{(1)} - V)\frac{1 - P_n^{(0)}}{E_n^{(0)} - H_0}V\Psi_n^{(0)} \qquad (17.40)$$

The relation (17.28) finally allows us to write $\Psi_n^{(2)}$ entirely in terms of the unperturbed system as

$$\Psi_n^{(2)} = -\frac{1 - P_n^{(0)}}{(E_n^{(0)} - H_0)^2}VP_n^{(0)}V\Psi_n^{(0)} + \frac{1 - P_n^{(0)}}{E_n^{(0)} - H_0}V\frac{1 - P_n^{(0)}}{E_n^{(0)} - H_0}V\Psi_n^{(0)} \qquad (17.41)$$

Exercise 17.1. Show that if $C_n^{(1)} = C_n^{(2)} = 0$,

$$(\Psi_n, V\Psi_n) = E_n^{(1)} + 2gE_n^{(2)} + O(g^2) \qquad (17.42)$$

Also evaluate $(\Psi_n, H_0\Psi_n)$ to second order in g. Does the sum of $(\Psi_n, H_0\Psi_n)$ and $(\Psi_n, gV\Psi_n)$ give E_n to second order in g?

Exercise 17.2. Calculate the normalization factor for the perturbed eigenvector to second order in g.

The perturbation theory can be further developed in this way to any desired order.[2] For practical purposes it is rarely necessary to go beyond the second order.

Exercise 17.3. Obtain expressions for the mth-order correction to the energy and the eigenvectors in terms of the corrections of lower order. Show that with the choice $C_n^{(k)} = 0$, for all $k > 0$, the perturbed eigenvector, instead of being normalized to unity, satisfies the condition

$$(\Psi_n^{(0)}, \Psi_n) = 1$$

Derive the formula for the energy shift,

$$\Delta E_n = E_n - E_n^{(0)} = (\Psi_n^{(0)}, V\Psi_n) \qquad (17.43)$$

4. Electrostatic Polarization and the Dipole Moment. As an important example we consider an electron bound in an atom and placed in a weak

[2] T. Kato, *Progr. of Theor. Phys.*, **4**, 514 (1949); K. A. Brueckner, *Phys. Rev.*, **100**, 36 (1955). As shown by R. M. Sternheimer in *Phys. Rev.* **84**, 244 (1951) and *Phys. Rev.* **95**, 736 (1954), it is sometimes practicable to solve the inhomogeneous perturbation equations directly without making an expansion in terms of unperturbed eigenfunctions.

uniform external electric field **E**. The field can be derived from an electrostatic potential

$$\phi(\mathbf{r}) = -\mathbf{E} \cdot \mathbf{r}$$

where the coordinate origin is most conveniently chosen at the position of the nucleus, and the perturbation potential is

$$gV = -e\phi = e\mathbf{E} \cdot \mathbf{r}$$

The energy of the system to second order is given by the formulas of the last section as

$$E_n = E_n^{(0)} + e\mathbf{E} \cdot \mathbf{r}_{nn} + e^2 \sum_{k \neq n} \frac{(\mathbf{E} \cdot \mathbf{r}_{nk})(\mathbf{E} \cdot \mathbf{r}_{kn})}{E_n^{(0)} - E_k^{(0)}} \qquad (17.44)$$

where all matrix elements are to be taken with respect to the unperturbed eigenstates.

The shift of energy levels in an electric field is known as the *Stark effect*. The first two terms of the perturbation expansion give accurate results for applied fields which are small compared to the internal electric field of the atom. The latter is in order of magnitude given by $E^{(0)}/ea \simeq 10^{10}$ volts/meter. In practice this condition is always well satisfied and successive terms in the perturbation expansion decrease rapidly and uniformly, except that some terms may vanish owing to certain symmetry properties of the system. The most important instance of this is conservation of parity which results in the absence of the first-order term in almost all atomic states, with the important exception of the excited states in hydrogenic atoms. If the unperturbed electron is in a central field, H_0 is invariant under coordinate inversion through the center of force, and the energy eigenstates may be taken to have definite parity. We saw in Section 16.10 that the expectation value of the operator **r**, which is odd under reflection, vanishes for states of definite parity; hence, the external electric field can, in general, produce no first-order, or linear, Stark effect. An exception arises if the central field is a pure Coulomb field (hydrogenic atoms) because the excited states of such atoms exhibit degeneracy of states with opposite parity. Superposition of such states yields energy eigenstates which have no definite parity, and the expectation value of **r** need no longer vanish. We shall resume discussion of the linear Stark effect of the first excited state of hydrogen as an example of degenerate perturbation theory in Section 17.6. The inevitable degeneracy of the magnetic substates for states of nonzero angular momentum, on the other hand, does not affect our conclusion concerning the absence of the linear Stark effect, because all these substates have the same parity (Section 16.10).

Usually, then, the first-order term in (17.44) is absent. The second-order term gives rise to the so-called *quadratic Stark effect*. If the electric field is

along the z-axis, the quadratic Stark effect is given by the formula

$$E_n = E_n^{(0)} + e^2 \mathbf{E}^2 \sum_{k \neq n} \frac{|z_{nk}|^2}{E_n^{(0)} - E_k^{(0)}} \tag{17.45}$$

The parity selection rule insures that the trivial degeneracy of magnetic substates does not interfere with the applicability of this formula, because two states which differ only by their magnetic quantum number have the same parity. By inspection of the work of the preceding section we see that such apparently indeterminate (0/0) terms may simply be omitted from the sum in (17.45).

Perturbation theory may also be used to calculate the expectation value of the static electric dipole moment, $-e\mathbf{r}$, in a stationary state of the one-electron atom. In the lowest approximation,

$$\mathbf{p}_0 = -e\mathbf{r}_{nn} = -e \int \mathbf{r} \, |\psi_n^{(0)}(\mathbf{r})|^2 \, d\tau \tag{17.46}$$

This is called the *permanent electric dipole moment* of the system, because it represents a vector which is determined by the unperturbed state of the system and entirely independent of the applied field. It vanishes, of course, for all states which possess definite parity.

A better approximation is obtained by using the correction (17.36):

$$\rho \approx |\psi_n^{(0)} + g\psi_n^{(1)}|^2 \approx |\psi_n^{(0)}|^2 + e\psi_n^{(0)*} \sum_{k \neq n} \psi_k^{(0)} \frac{\mathbf{E} \cdot \mathbf{r}_{kn}}{E_n^{(0)} - E_k^{(0)}}$$

$$+ e\psi_n^{(0)} \sum_{k \neq n} \psi_k^{(0)*} \frac{\mathbf{E} \cdot \mathbf{r}_{kn}}{E_n^{(0)} - E_k^{(0)}} \tag{17.47}$$

The last two terms describe the polarization of the atom by the applied field.

In this approximation we obtain for the dipole moment of the one-electron atom

$$\mathbf{p} = -e \int \rho \mathbf{r} \, d\tau = \mathbf{p}_0 - e^2 \sum_{k \neq n} \frac{\mathbf{r}_{nk}\mathbf{r}_{kn} + \mathbf{r}_{kn}\mathbf{r}_{nk}}{E_n^{(0)} - E_k^{(0)}} \cdot \mathbf{E}$$

where the last term represents the *induced dipole moment* in the state n,

$$\mathbf{p}_1 = e^2 \sum_{k \neq n} \frac{\mathbf{r}_{nk}\mathbf{r}_{kn} + \mathbf{r}_{kn}\mathbf{r}_{nk}}{E_k^{(0)} - E_n^{(0)}} \cdot \mathbf{E} = \boldsymbol{\alpha} \cdot \mathbf{E} \tag{17.48}$$

This equation defines a *tensor* (or dyadic) *of polarizability* for the state n,

$$\boldsymbol{\alpha} = e^2 \sum_{k \neq n} \frac{\mathbf{r}_{nk}\mathbf{r}_{kn} + \mathbf{r}_{kn}\mathbf{r}_{nk}}{E_k^{(0)} - E_n^{(0)}} \tag{17.49}$$

It is of interest to note that this tensor is symmetric.[3] In many applications we find $\alpha_{xy} = \alpha_{yz} = \alpha_{zx} = 0$, and $\alpha_{xx} = \alpha_{yy} = \alpha_{zz}$, so that the polarizability is a scalar.

Exercise 17.4. Calculate the polarizability of an isotropic harmonic oscillator from (17.49), and verify that the result agrees with an exact calculation of the induced dipole moment.

Note that

$$\mathbf{E} \cdot \mathbf{p} = -\int \psi_n{}^* g V \psi_n \, d\tau = \mathbf{E} \cdot \mathbf{p_0} + \mathbf{E} \cdot \boldsymbol{\alpha} \cdot \mathbf{E} + O(\mathbf{E}^3)$$

Comparing this with (17.42), we obtain

$$E_n = E_n^{(0)} - \mathbf{E} \cdot \mathbf{P_0} - \tfrac{1}{2}\mathbf{E} \cdot \boldsymbol{\alpha} \cdot \mathbf{E} + \cdots$$

which upon substitution of $\mathbf{p_0}$ and $\boldsymbol{\alpha}$ can easily be seen to be identical with (17.44). The factor of $\frac{1}{2}$ which appears in the energy owing to the induced dipole moment is the same as that customarily found when "stress" (**E**) and "strain" ($\mathbf{p_1}$) are proportional, as is the case in the approximation leading to (17.48).

The rigorous evaluation of the sums over unperturbed states, which are encountered in all higher order perturbation calculations, is usually a difficult problem. However, sometimes special techniques may allow such sums to be performed. As an example consider the quadratic Stark effect or the polarizability of the ground state of the hydrogen atom. According to (17.44) and (17.49), this requires the evaluation of

$$\sum_{k \neq 0} \frac{|z_{0k}|^2}{E_0^{(0)} - E_k^{(0)}} = \sum_{k \neq 0} \frac{z_{0k} z_{k0}}{E_0^{(0)} - E_k^{(0)}}$$

where the subscript 0 labels the ground state of hydrogen $|0\rangle$ and k labels all other states of hydrogen.

Let us suppose that it is possible to find, by whatever procedure, an operator F which satisfies the equation

$$z |0\rangle = (FH_0 - H_0 F) |0\rangle \tag{17.50}$$

Then we have

$$z_{k0} = \langle k| z |0\rangle = \langle k| FH_0 |0\rangle - \langle k| H_0 F |0\rangle = (E_0^{(0)} - E_k^{(0)})\langle k| F |0\rangle$$

[3] M. Born and E. Wolf, *Principles of Optics*, 3rd ed., Pergamon Press, New York, 1965, p. 366. See also W K. H. Panofsky and M. Phillips, *Classical Electricity and Magnetism*, 2nd ed., Addison-Wesley Publishing Company, Reading, 1962, p. 30 and Section 6-2.

and

$$\sum_{k \neq 0} \frac{|z_{0k}|^2}{E_0^{(0)} - E_k^{(0)}} = \sum_{k \neq 0} \langle 0| z |k\rangle\langle k| F |0\rangle = \langle 0| zF |0\rangle - \langle 0| z |0\rangle\langle 0| F |0\rangle$$

(17.51)

By the use of closure in the last step the sum over states has thus been transformed into the calculation of expectation values in a single state. Of course, the usefulness of (17.51) hinges on our ability to determine the operator F.[4]

If H_0 stands for the Hamiltonian of the unperturbed hydrogen atom and $|0\rangle$ for the ground state of hydrogen, it is easy to determine F by writing (17.50) explicitly in the coordinate representation. Assuming that F is a function of the coordinates only (and not of the momenta), a differential equation for F is obtained, which is conveniently expressed in terms of spherical polar coordinates and may be solved by separation of variables. The details of the calculation are left to the reader, who may also verify by direct substitution that

$$F = - \frac{\mu a}{\hbar^2} \left(\frac{r}{2} + a \right) z$$

(17.52)

(where a = Bohr radius) satisfies (17.50) in our example.

Since the expectation value of z in the ground state of hydrogen vanishes, it follows from (17.51) that

$$\sum_{k \neq 0} \frac{|z_{0k}|^2}{E_0^{(0)} - E_k^{(0)}} = - \frac{\mu a}{\hbar^2} \langle 0| \left(\frac{r}{2} + a \right) z^2 |0\rangle$$

The remaining expectation value is easily evaluated by noting that by virtue of the spherical symmetry of the ground state (S-state)

$$\langle 0| f(r)z^2 |0\rangle = \langle 0| f(r)x^2 |0\rangle = \langle 0| f(r)y^2 |0\rangle = \tfrac{1}{3}\langle 0| f(r)r^2 |0\rangle$$

Hence,

$$\sum_{k \neq 0} \frac{|z_{0k}|^2}{E_0^{(0)} - E_k^{(0)}} = - \frac{\mu a}{3\hbar^2} (\tfrac{1}{2}\langle r^3 \rangle_0 + a\langle r^2 \rangle_0)$$

But

$$\langle r^n \rangle_0 = \frac{1}{\pi a^3} \int d\Omega \int_0^\infty r^{n+2} \exp\left(- \frac{2r}{a} \right) dr = \frac{a^n}{2^{n+1}} (n + 2)!$$

We thus finally obtain

$$E_0 = - \frac{e^2}{2a} - \frac{9}{4} a^3 |\mathbf{E}|^2$$

(17.53)

[4] Ingenious use was made of this method by A. Dalgarno and J. T. Lewis, *Proc. Roy. Soc.*, A **233**, 70 (1955). For earlier polarizability calculations, based on direct solutions of the inhomogeneous equations arising in perturbation theory, see H. M. Foley, O. M. Sternheimer, and D. Tycko, *Phys. Rev.* **93**, 734 (1954), and R. M. Sternheimer, *Phys. Rev.* **96**, 951 (1954) and *Phys. Rev.* **127**, 1220 (1962).

for the ground state of the hydrogen atom to second order in the applied electric field.[5] The presence of the field causes a lowering of the ground state energy. This was to be expected from (17.39), since every term in the sum may be regarded as a repulsion of the nth level by the kth level.

5. Degenerate Perturbation Theory. We must now supplement our perturbation methods by admitting the possibility that the nth unperturbed state may be degenerate, usually as the result of certain symmetries. Thus, if the system is in a central force field, the magnetic substates of a given angular momentum all have the same energy, owing to rotational symmetry. If this symmetry is disturbed, as by the application of a magnetic field, the degeneracy is usually removed.

The perturbation procedure developed in Sections 17.1 and 17.3 cannot be applied without modification, because the expansion (17.7) of the eigenvector was based of the assumption that we know into which unperturbed eigenvector $\Psi_n^{(0)}$ the exact perturbed eigenvector Ψ_n collapses as g approaches zero. This assumption breaks down when the unperturbed state is degenerate and we have no prior knowledge which would allow us to predict what particular linear combination of the given degenerate substates the eigenvector Ψ_n will go into as $g \to 0$. (However, frequently symmetry properties can be used to avoid this ambiguity. For the resulting simplifications see below.)

The breakdown of the simple Rayleigh-Schrödinger theory in the case of degenerate unperturbed states appears formally as the vanishing of some of the energy denominators in (17.36) and (17.39). When this happens, the perturbation expansions become meaningless (except if $V_{kn} = 0$ as a result of some symmetry). For practical applications it is important to realize that these difficulties arise not only if the unperturbed states are strictly degenerate, but also if they are merely so close in energy that $|V_{kn}/(E_n^{(0)} - E_n^{(0)})|$ is large and causes large-scale mixing of unperturbed states in (17.36).

In order to keep the notation uncluttered, let us suppose that the unperturbed eigenvalue $E_n^{(0)}$ is only doubly degenerate, i.e., that two linearly independent eigenvectors $\Psi_{n1}^{(0)}$ and $\Psi_{n2}^{(0)}$ belong to it. We may assume these two eigenvectors to be orthonormal. When the perturbation is "turned on," the level usually splits into two components, and we have the expansions,

$$E_{n1} = E_n^{(0)} + gE_{n1}^{(1)} + g^2E_{n1}^{(2)} + \cdots \qquad (17.54a)$$

$$E_{n2} = E_n^{(0)} + gE_{n2}^{(1)} + g^2E_{n2}^{(2)} + \cdots \qquad (17.54b)$$

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[5] An alternative method for obtaining the result (17.53) consists of using parabolic coordinates in which the Schrödinger equation for the hydrogen atom is separable even in the presence of a uniform electric field.