Since we are interested only in terms of order H'^2, we expand the denominator of (32.18) to obtain

$$(E_0 + 2A\langle 0|H'^2|0\rangle)(1 + A^2\langle 0|H'^2|0\rangle)^{-1} \approx E_0 + (2A - E_0A^2)\langle 0|H'^2|0\rangle \quad (32.19)$$

If we remember that E_0 is negative, we find that (32.19) has a minimum with respect to variation of A when $A = 1/E_0$, in which case (32.17) becomes

$$E_0 + W(R) \leq E_0 + \frac{\langle 0|H'^2|0\rangle}{E_0} = E_0 - \frac{6e^2a_0^5}{R^6} \quad (32.20)$$

Thus in (32.16) and (32.20) we have both upper and lower limits on the interaction energy:

$$-\frac{8e^2a_0^5}{R^6} \leq W(R) \leq -\frac{6e^2a_0^5}{R^6} \quad (32.21)$$

More careful variation calculations have shown that the numerical coefficient in $W(R)$ is very nearly 6.50.[1]

33□ALTERNATIVE TREATMENT OF THE PERTURBATION SERIES

We have seen in Sec. 32 how the expression (31.11) for the second-order perturbed energy can give a useful limit even when the generalized summation S cannot be carried out. In some situations, however, closed-form expressions for W_2 and ψ_1, both of which otherwise involve infinite summations, can be obtained. We illustrate this first with the problem of the second-order Stark effect of a hydrogen atom in its ground state and then generalize the procedure to a wider class of situations.

SECOND-ORDER STARK EFFECT IN HYDROGEN

The ground state of a hydrogen atom is nondegenerate, and the first-order perturbed energy in a uniform external electric field is zero. Our problem then is to calculate Eq. (31.11):

$$W_2 = \mathsf{S}'_n \frac{|\langle 0|H'|n\rangle|^2}{E_0 - E_n} \quad (33.1)$$

[1] See L. Pauling and E. B. Wilson, Jr., "Introduction to Quantum Mechanics," sec. 47a (McGraw-Hill, New York, 1935). The result (32.21) is not strictly correct, since H' in (32.12) included only the static dipole-dipole interaction between the two atoms. In reality, there is also an effect of retardation, which arises from the finite speed of propagation of the electromagnetic interaction between the two dipoles. This causes $W(R)$ to fall off like $-1/R^7$ when R is large in comparison with the electromagnetic wavelength associated with an atomic transition frequency: $R \gg \hbar c a_0/e^2 = 137a_0$. At such large distances the interaction is uninterestingly small, so that (32.21) actually provides useful limits on $W(R)$. See H. B. G. Casimir and D. Polder, *Phys. Rev.* **73**, 360 (1948).

The ground state ket $|0\rangle$ in the coordinate representation is

$$\langle \mathbf{r}|0\rangle = u_{100}(\mathbf{r}) = (\pi a_0{}^3)^{-\frac{1}{2}} e^{-r/a_0},$$

and $E_0 = -e^2/2a_0$. Equation (33.1) and the variation method are used in Prob. 9 to obtain lower and upper bounds, respectively, for W_2.

Instead of working directly with Eq. (33.1), we shall first find ψ_1 by solving the second of Eqs. (31.4) subject to the condition (31.6), and then make use of (31.7).[1] With H' given by (31.26), $W_1 = 0$, and the second of Eqs. (31.4) is an inhomogeneous differential equation for ψ_1:

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{r} - E_0\right)\psi_1 = -e\mathsf{E}r\cos\theta\, u_{100} \tag{33.2}$$

We show first that the only angle dependence of ψ_1 is through a multiplying factor $\cos\theta$. One way of seeing this is to expand ψ_1 as a series of functions of r times spherical harmonics in θ, ϕ and to note that each term is an eigenfunction of the angular part of ∇^2. Then the left side of (33.2) is a similar series of spherical harmonics, and the only term we wish to retain is that which has the same angular dependence as the right side: $Y_{10}(\theta,\phi)$ or $\cos\theta$. An alternative way of seeing the same thing is to note that ψ_1 given by (31.9) is a sum over only those unperturbed states u_n for which $a_n{}^{(1)}$ fails to vanish; in accordance with (31.10), this means that u_n is proportional to $\cos\theta$ since the unperturbed state is spherically symmetrical. Thus each term in the series for ψ_1 is proportional to $\cos\theta$, and hence ψ_1 is also.

We can thus write

$$\psi_1(\mathbf{r}) = f(r)\cos\theta \tag{33.3}$$

and Eq. (31.6) is automatically satisfied. Substitution of (33.3) into (33.2) gives

$$\frac{d^2f}{dr^2} + \frac{2}{r}\frac{df}{dr} - \frac{2}{r^2}f + \frac{2}{a_0 r}f - \frac{1}{a_0{}^2}f = \frac{2\mathsf{E}}{ea_0(\pi a_0{}^3)^{\frac{1}{2}}} re^{-r/a_0} \tag{33.4}$$

The solution of Eq. (33.4) is expected to have the form of a power series in r multiplied by e^{-r/a_0}; further, the series is expected to start with the first or higher power of r, since otherwise (33.3) will be singular at the origin. It turns out that the series terminates after two terms, so that the solution of (33.4) is

$$f(r) = -(\pi a_0{}^3)^{-\frac{1}{2}}\frac{\mathsf{E}}{e}(a_0 r + \tfrac{1}{2}r^2)e^{-r/a_0} \tag{33.5}$$

[1] This approach appears to have been first published by M. Kotani, "Quantum Mechanics," vol. I, p. 127 (Yuwanami Book Co., Tokyo, 1951).

as may be verified by substitution. Thus the wave function that is correct through first order in E is

$$(\pi a_0^3)^{-\frac{1}{2}} e^{-r/a_0} \left[1 - \frac{\mathsf{E}}{e} (a_0 r + \tfrac{1}{2} r^2) \cos\theta \right] \tag{33.6}$$

Substitution of the expression for ψ_1 obtained from Eqs. (33.3) and (33.5) into (31.7) gives for the second-order perturbed energy

$$\begin{aligned} W_2 &= e\mathsf{E}(\pi a_0^3)^{-\frac{1}{2}} \int r \cos^2\theta f(r) e^{-r/a_0}\, d^3r \\ &= -\frac{4\mathsf{E}^2}{3a_0^3} \int_0^\infty (a_0 r^4 + \tfrac{1}{2} r^5) e^{-2r/a_0}\, dr \\ &= -\frac{9}{4} \mathsf{E}^2 a_0^3 \end{aligned} \tag{33.7}$$

This expression for the second-order Stark effect was first obtained by separation of the wave equation in parabolic coordinates.[1]

POLARIZABILITY OF HYDROGEN

It was remarked at the end of Sec. 31 that the second-order Stark effect could be interpreted in terms of an induced electric dipole moment. This induced moment is proportional to the applied electric field and in the same direction, and the ratio α of dipole moment to field strength is called the *polarizability*. It is easily seen that these conditions hold exactly for a charged isotropic harmonic oscillator and that the energy change in this case is $-\frac{1}{2}\alpha\mathsf{E}^2$ (Prob. 1). For a general system, in which the energy change is not exactly proportional to E^2, it is still true that

$$W_2 = -\tfrac{1}{2}\alpha\mathsf{E}^2 \tag{33.8}$$

Comparison of Eqs. (33.7) and (33.8) shows that

$$\alpha = \tfrac{9}{2} a_0^3 \tag{33.9}$$

for a hydrogen atom its ground state (see Prob. 12).

[1] G. Wentzel, *Z. Physik* **38,** 518 (1926); I. Waller, *Z. Physik* **38,** 635 (1926); P. S. Epstein, *Phys. Rev.* **28,** 695 (1926). The general expression for the first- and second-order Stark effect with nuclear charge Z, in terms of the parabolic quantum numbers of Sec. 16, is $\frac{3}{2}n(n_1 - n_2)(e\mathsf{E}a_0/Z) - (\mathsf{E}^2 a_0^3/16Z^4)n^4[17n^2 - 3(n_1 - n_2)^2 - 9m^2 + 19]$. It should be noted that such a series in powers of E cannot converge since, strictly speaking, the system has no bound states. This is so because the electron of a hydrogen atom placed in a uniform electric field can gain enough energy by moving in the direction $-\mathsf{E}$ to compensate for its binding energy. In other words, the electron can tunnel through the potential barrier created by the nuclear coulomb field and the external electric field, as discussed in Sec. 17. The rate of spontaneous dissociation for a hydrogen atom in an electric field was calculated by J. R. Oppenheimer, *Phys. Rev.* **31,** 66 (1928), and is exceedingly small for fields of laboratory strength. Even though the series for the perturbed energy in powers of E does not converge, it is useful for ordinary field strengths.

METHOD OF DALGARNO AND LEWIS

The foregoing procedure can be generalized in the following way.[1] We start with Eq. (31.11), which is applicable to the ground state of any system since in all known cases this state is nondegenerate:

$$W_2 = \mathsf{S}'_n \frac{\langle 0|H'|n\rangle\langle n|H'|0\rangle}{E_0 - E_n} \tag{33.10}$$

Suppose now that an operator F can be found such that

$$\frac{\langle n|H'|0\rangle}{E_0 - E_n} = \langle n|F|0\rangle \tag{33.11}$$

for all states n other than the ground state. Substitution into (33.10) then gives

$$W_2 = \mathsf{S}'_n\langle 0|H'|n\rangle\langle n|F|0\rangle = \langle 0|H'F|0\rangle - \langle 0|H'|0\rangle\langle 0|F|0\rangle \tag{33.12}$$

where the term $n = 0$ has first been added in to make the summation complete and then subtracted out. Thus, if F can be found, the evaluation of W_2 is greatly simplified, since only integrals over the unperturbed ground-state wave function need be evaluated.

Equation (33.11) can be written as

$$\langle n|H'|0\rangle = (E_0 - E_n)\langle n|F|0\rangle = \langle n|[F,H_0]|0\rangle$$

which is evidently valid if F satisfies the operator equation

$$[F,H_0] = H' + C$$

where C is any constant. However, this last equation is unnecessarily general; it is enough that F satisfy the much simpler equation

$$[F,H_0]|0\rangle = H'|0\rangle + C|0\rangle \tag{33.13}$$

from which it follows that $C = -\langle 0|H'|0\rangle$.

We now define a new ket $|1\rangle$, which is the result of operating on $|0\rangle$ with F. Then Eq. (33.13) may be written

$$(E_0 - H_0)|1\rangle = H'|0\rangle - \langle 0|H'|0\rangle|0\rangle \qquad \text{where} \qquad |1\rangle \equiv F|0\rangle \tag{33.14}$$

The ket $|1\rangle$ can evidently have an arbitrary multiple of $|0\rangle$ added to it; we choose this multiple so that $\langle 0|1\rangle = 0$. If now Eq. (33.14), which is an inhomogeneous differential equation, can be solved for $|1\rangle$, the second-order perturbed energy (33.12) can be written in terms of it as

$$W_2 = \langle 0|H'|1\rangle \tag{33.15}$$

[1] A. Dalgarno and J. T. Lewis, *Proc. Roy. Soc. (London)* **A233,** 70 (1955); C. Schwartz, *Ann. Phys. (N.Y.)* **6,** 156 (1959).

In similar fashion the series (31.9) for ψ_1 can be written in closed form:

$$\begin{aligned}\psi_1 &= \mathsf{S}'_n \frac{|n\rangle\langle n|H'|0\rangle}{E_0 - E_n} = \mathsf{S}'_n |n\rangle\langle n|F|0\rangle \\ &= F|0\rangle - |0\rangle\langle 0|F|0\rangle = |1\rangle \end{aligned} \tag{33.16}$$

It is apparent that Eqs. (33.15) and (33.16) are consistent with Eq. (31.7), as of course they must be.

The Dalgarno-Lewis method thus replaces the evaluation of the infinite summation (31.9) by the solution of the inhomogeneous differential equation (33.14). The latter procedure may be much simpler even when it cannot be done in closed form, as with (33.4).

THIRD-ORDER PERTURBED ENERGY

The ket $|1\rangle = F|0\rangle$ is all that is needed to find the third-order perturbed energy W_3. We make use of Eqs. (31.7), (31.12), (31.13), and the complex conjugate of (33.11) to write

$$\begin{aligned} W_3 &= (u_0, H'\psi_2) \\ &= \mathsf{S}'_k \frac{\langle 0|H'|k\rangle}{E_0 - E_k} \left(\mathsf{S}'_n \frac{\langle k|H'|n\rangle\langle n|H'|0\rangle}{E_0 - E_n} - \frac{\langle k|H'|0\rangle\langle 0|H'|0\rangle}{E_0 - E_k} \right) \\ &= \mathsf{S}'_k \langle 0|F^\dagger|k\rangle (\mathsf{S}'_n \langle k|H'|n\rangle\langle n|F|0\rangle - \langle k|F|0\rangle\langle 0|H'|0\rangle) \\ &= \langle 0|F^\dagger H'F|0\rangle - \langle 0|F^\dagger|0\rangle\langle 0|H'F|0\rangle - \langle 0|F^\dagger H'|0\rangle\langle 0|F|0\rangle \\ &\qquad - \langle 0|F^\dagger F|0\rangle\langle 0|H'|0\rangle + 2\langle 0|F^\dagger|0\rangle\langle 0|H'|0\rangle\langle 0|F|0\rangle \\ &= \langle 1|H'|1\rangle - \langle 1|1\rangle\langle 0|H'|0\rangle \end{aligned} \tag{33.17}$$

since $\langle 0|1\rangle = 0$. We thus obtain a closed expression for W_3 as well.[1]

INTERACTION OF A HYDROGEN ATOM AND A POINT CHARGE

As an example of this method, we now calculate the change in energy of a hydrogen atom in its ground state when a point charge Ze is placed at a fixed distance R. The perturbation is

$$\begin{aligned} H' &= \frac{Ze^2}{R} - \frac{Ze^2}{(R^2 + r^2 - 2Rr\cos\theta)^{\frac{1}{2}}} \\ &= -\frac{Ze^2}{R} \sum_{l=1}^{\infty} \left(\frac{r}{R}\right)^l P_l(\cos\theta) \end{aligned} \tag{33.18}$$

provided that $R > r$ or, equivalently, that R is much greater than a_0.

[1] This result can also be obtained directly from Eqs. (31.4) and (31.6) as a special case of the formula derived in Prob. 14.

From the structure of Eq. (33.14), we expect that the coordinate representation of the ket $|1\rangle$ can be written in the form

$$\langle \mathbf{r}|1\rangle = \sum_{l=1}^{\infty} f_l(r) P_l(\cos\theta) \tag{33.19}$$

Substitution of (33.19) into (33.14) leads to the following differential equation for $f_l(r)$:

$$\frac{d^2 f_l}{dr^2} + \frac{2}{r}\frac{df_l}{dr} - \frac{l(l+1)}{r^2} f_l + \frac{2}{a_0 r} f_l - \frac{1}{a_0^2} f_l = -\frac{2Z}{a_0 R^{l+1}(\pi a_0^3)^{\frac{1}{2}}} r^l e^{-r/a_0} \tag{33.20}$$

As expected, this agrees with Eq. (33.14) when we put $l = 1$ and $\mathsf{E} = -Ze/R^2$.

A solution of Eq. (33.20) is easily found in analogy with (33.5) and again contains only two terms. Substitution into (33.19) gives

$$\langle \mathbf{r}|1\rangle = \sum_{l=1}^{\infty} \frac{Z}{R^{l+1}(\pi a_0^3)^{\frac{1}{2}}} \left(\frac{a_0 r^l}{l} + \frac{r^{l+1}}{l+1} \right) e^{-r/a_0} P_l(\cos\theta) \tag{33.21}$$

which, in accordance with (33.16), is equal to $\psi_1(\mathbf{r})$. Similarly, Eq. (33.15) shows that W_2 is given by

$$W_2 = \langle 0|H'|1\rangle = -Z^2 e^2 \sum_{l=1}^{\infty} \frac{(l+2)(2l+1)!}{l 2^{2l+1}} \frac{{a_0}^{2l+1}}{R^{2l+2}} \tag{33.22}$$

Again, the leading term ($l = 1$) agrees with (33.7) when $\mathsf{E} = -Ze/R^2$.

It should be noted that, although Eq. (33.22) gives the first two terms of an asymptotic series in $1/R$ correctly, the third term, which is proportional to $1/R^8$, is dominated by the leading term of W_3. Equation (33.17) shows that $W_3 = \langle 1|H'|1\rangle$ in this case and that the leading term for large R is proportional to $1/R^7$ (see Prob. 15).[1]

34□THE WKB APPROXIMATION

In the development of quantum mechanics, the Bohr-Sommerfeld quantization rules of the old quantum theory (Sec. 2) occupy a position intermediate between classical and quantum mechanics. It is interesting that there is a method for the approximate treatment of the Schrödinger wave

[1] A. Dalgarno and A. L. Stewart, *Proc. Roy. Soc.* (*London*) **A238,** 276 (1956). It should be noted that, unlike the situation with the van der Waals interaction discussed in the preceding section, there is no correction arising from retardation in the present problem. This is because the only motion is that of a single electron in the electrostatic potential of two fixed charges.