

Physics 221A
Fall 1996
Notes 19
The Stark Effect in Hydrogen
and Alkali Atoms

In these notes we will consider the Stark effect in hydrogen and alkali atoms as a physically interesting example of bound state perturbation theory. The Stark effect concerns the behavior of atoms in external electric fields.

We begin with the one-electron Hamiltonian

$$H_0 = \frac{p^2}{2m} + V_0(r). \quad (19.1)$$

Here $V_0(r)$ is a central force potential, which for hydrogen is

$$V_0(r) = -\frac{e^2}{r}. \quad (19.2)$$

Neutral alkali atoms such as Na have one electron in the outer, valence shell, which surrounds a core of completely filled subshells containing $Z-1$ electrons. A simple model of such atoms treats the inner core as a spherically symmetric distribution of negative charge which screens the nuclear charge. The amount of screening depends on the radius; as $r \rightarrow 0$, the full, unscreened charge of the nucleus is seen, whereas when the valence electron is pulled far away from the core, it leaves behind an ion of $+1$ unit of charge. Thus, we can use Gauss' law to find the electric field (radial component only) seen by the valence electron,

$$E_0(r) = \frac{eZ_{\text{eff}}(r)}{r^2}, \quad (19.3)$$

where

$$Z_{\text{eff}}(r) \rightarrow \begin{cases} Z, & r \rightarrow 0, \\ 1, & r \rightarrow \infty. \end{cases} \quad (19.4)$$

This gives the potential for the valence electron,

$$V_0(r) = -e^2 \int_r^\infty \frac{Z_{\text{eff}}(r)}{r^2} dr, \quad (19.5)$$

which can be used in the Hamiltonian (19.1). There is no simple formula for $Z_{\text{eff}}(r)$.

For weak external electric fields it would be necessary to include the effects of spin in the Hamiltonian (19.1), not because the spin interacts with the external electric field (it does

not), but because the spin affects the energy levels and degeneracies of the unperturbed system through the fine structure splittings, the Lamb shift, etc. If the external field is sufficiently strong, however, the Stark effect overwhelms the fine structure and other small splittings, and the spin can be ignored. In the following we will ignore the spin and treat the electron as if it were a spinless particle; we do this partly for simplicity, but the approach is realistic for strong enough fields.

Before embarking on perturbation theory, we must understand the unperturbed system, its energies, eigenstates and their degeneracies. In our spinless model, the unperturbed energy levels in hydrogen are given by the usual Bohr formula,

$$E_n = -\frac{1}{2n^2} \frac{e^2}{a_0}, \quad (19.6)$$

where a_0 is the Bohr radius. These levels are n^2 -fold degenerate. In the case of the alkalis, the energy levels have the form $E_{n\ell}$, and are $(2\ell + 1)$ -fold degenerate. There is no simple formula for the alkali levels $E_{n\ell}$, but for given n , the energies are an increasing function of ℓ . For example, in Na, the ground state is a $3s$ level ($n = 3$, $\ell = 0$), and the $3p$ level ($n = 3$, $\ell = 1$) is sufficiently far above the ground state that the photon emitted in the transition $3p \rightarrow 3s$ lies in the optical range of frequencies (this is the yellow sodium D -line). In both cases (hydrogen and alkalis) the energy eigenstates have the form $|n\ell m\rangle$.

Any system with rotational invariance, regardless of the number of particles or the presence of spin-dependent interactions, has energy levels which are independent of the quantum number m of J_z , the z -component of the total angular momentum. In particular, in central force problems, where the energy eigenstates have the form $|n\ell m\rangle$, the energy levels in general have the form $E_{n\ell}$, and are $(2\ell + 1)$ -fold degenerate, corresponding to $m = -\ell, \dots, +\ell$. This is the situation with the alkalis. In hydrogen, however, the energies have additional degeneracy, that is, they are independent of both m and ℓ , and the n^2 degeneracy comes from counting all $\ell = 0, \dots, n - 1$ and $m = -\ell, \dots, +\ell$. All central force Hamiltonians are invariant under rotations in 3-dimensional space. The Coulomb Hamiltonian, however, is actually invariant under rotations in a certain 4-dimensional space, in which the extra dimension cannot be interpreted in the same physical sense as the first three. It is this larger symmetry which is responsible for the extra degeneracy seen in hydrogen.

As for the perturbation, let us write \mathbf{F} for the external electric field (instead of \mathbf{E} , to avoid confusion with the energy E), and let us take it to lie in the z -direction,

$$\mathbf{F} = F\hat{z}. \quad (19.7)$$

Thus, the perturbing potential has the form

$$V_1 = q\phi = -q\mathbf{F} \cdot \mathbf{r} = eFz, \quad (19.8)$$

where we set $q = -e$ for the electron. The unperturbed potential V_0 depends on r , but the perturbing potential V_1 depends on z , so the perturbation breaks the full rotational symmetry of the unperturbed problem. However, the perturbed Hamiltonian is still invariant under rotations about the z -axis.

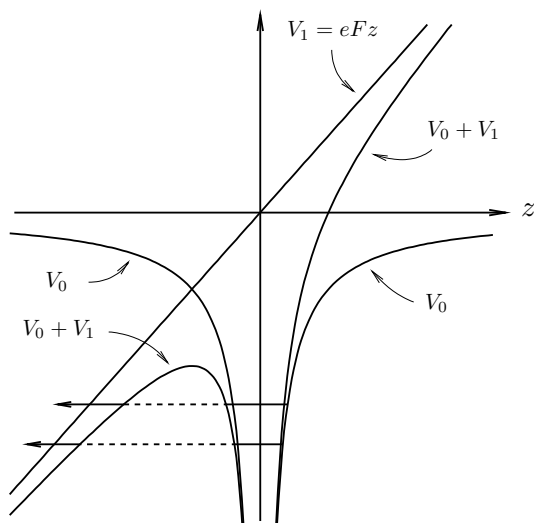


Fig. 19.1. The total potential energy $V_0 + V_1$ along the z -axis for an atomic electron in the Stark effect. The atomic states which are bound in the absence of the external field become resonances (dotted lines) when the perturbation is turned on.

Figure 19.1 is a plot of the total potential $V_0 + V_1$ along the z -axis, which reveals several qualitative features of the exact solution. For small z , the attractive Coulomb field dominates the total potential, and we have the usual Coulomb well which supports atomic bound states. We assume the applied electric field F is small compared to the electric field due to the nucleus in this region, which justifies the use of perturbation theory. However, for large negative z , the unperturbed potential goes to zero, while the perturbing potential becomes large and negative. At intermediate values of negative z , the competition between the two potentials gives a maximum in the total potential. The bound states of the unperturbed system are able to tunnel through the potential barrier, as indicated by the dotted lines in the figure. We see that when an external electric field is turned on, the bound states of the atom cease to be bound in the strict sense, and become resonances.

This happens regardless of how weak the external field is. Obviously this is because an electron can gain an arbitrarily large amount of energy in an uniform field if we are willing to move it far enough, and this energy can be larger than the binding energy of the atom. Electrons which tunnel through the barrier and emerge into the classically allowed region at large negative z will accelerate in the external field, leaving behind an ion. This is the phenomenon of *field ionization*.

However, the time scale for this tunnelling may be very long. As we know from WKB theory, the tunneling probability is exponentially small in the tunnelling action, so we expect the deeper bound states to have longer lifetimes in the external field, perhaps extremely long lifetimes. Furthermore, as the strength of the electric field is decreased, the distance the electron must tunnel increases, and the tunnelling probability decreases exponentially. On the other hand, the atom has an infinite number of very weakly bound states which pile up at $E = 0$, and many of these will lie above the top of the barrier when the external field is turned on. These states of course no longer exist, even as resonances, in the presence of the perturbation. This simply means that the weakly bound states are easily ionized.

In the following perturbation analysis, we will see no evidence of the tunnelling. As we know, a resonance can be thought of as an energy level which has both a real and an imaginary part; as we will see, bound state perturbation theory will only give us the shift in the real parts of the energy levels under the perturbation. The imaginary parts can be computed by various means, such as WKB theory, time-dependent perturbation theory, or (in the case of hydrogen) an exact separation of the wave equation in confocal parabolic coordinates.

For simplicity, let us begin the perturbation analysis with the ground state of the atom, so we can use nondegenerate perturbation theory. In the case of hydrogen, the ground state is the $1s$ or $|n\ell m\rangle = |100\rangle$ level, and for an alkali, the ground state has the form $|n00\rangle$ (for example, $n = 3$ for Na). According to Eq. (18.20) (with a change of notation), the first order shift in the ground state energy level is given by

$$\Delta E_{\text{gnd}}^{(1)} = \langle n00 | eFz | n00 \rangle = 0, \quad (19.9)$$

which vanishes because of parity. The operator z is odd under parity, while the state $|n00\rangle$ is one of a definite parity (even), so the matrix element vanishes. The matrix elements are the same as in the theory of electric dipole radiative transitions, and follow the same selection rules (here Laporte's rule). As we say, there is no linear Stark effect in the ground state of hydrogen or the alkalis.

More generally, there is no linear Stark effect in any nondegenerate eigenstate of any

system which conserves parity, since any such eigenstate must necessarily be an eigenstate of parity. (See Theorem 1.2.) This applies to multiparticle systems, as well as the single particle systems considered here. Since the Hamiltonians for all isolated atoms, molecules and nuclei conserve parity to a high degree of approximation, we can say that there is no linear Stark effect for any nondegenerate eigenstate of such a system. The weak interactions do violate parity, and cause the energy eigenstates of real systems to contain small admixtures of states of opposite parity, but these effects are very small and are difficult to see even when one is looking for them. (Weak interactions are easier to see at higher energies.) In the following discussion we will ignore the weak interactions, and proceed as if all Hamiltonians of interest do commute with parity.

The vanishing of the linear Stark effect is closely related to the vanishing of a permanent electric dipole moment. In classical electromagnetic theory, we define the dipole moment vector \mathbf{d} of a charge distribution by

$$\mathbf{d} = \int d^3\mathbf{r} \rho(\mathbf{r})\mathbf{r}, \quad (19.10)$$

that is, it is the charge-weighted position vector. In quantum mechanics, we replace $\rho(\mathbf{r})$ by $q|\psi(\mathbf{r})|^2$, and obtain the expectation value of the dipole moment operator,

$$\langle \mathbf{d} \rangle = \int d^3\mathbf{r} \psi(\mathbf{r})^* (q\mathbf{r})\psi(\mathbf{r}), \quad (19.11)$$

where the operator itself is given by

$$\mathbf{d} = q\mathbf{r}. \quad (19.12)$$

This is for a single charged particle; for several charged particles the dipole operator is defined by

$$\mathbf{d} = \sum_i q_i \mathbf{r}_i. \quad (19.13)$$

A quantum state is considered to have a permanent electric dipole moment if the expectation value (19.11) is nonzero. The integral in Eq. (19.11) has the same form as the matrix element occurring in Eq. (19.9), so we see that there is no permanent electric dipole moment in any nondegenerate eigenstate of any atom, molecule, or nucleus.

It is sometimes stated that molecules come in two kinds, those which have no permanent electric dipole moments, and those which do. The latter class includes molecules such as water H_2O and hydrogen chloride HCl . Let us keep these polar molecules in mind as we search for a system with a nonvanishing linear Stark effect.

Since nondegenerate energy eigenstates give no permanent electric dipole moment, let us look at degenerate eigenstates, starting with the excited states of the alkalis, which are

simpler than the excited states in hydrogen. The energy levels have the form $E_{n\ell}$, and the eigenstates $|n\ell m\rangle$ are $(2\ell + 1)$ -fold degenerate, because the energy does not depend on m . According to degenerate perturbation theory [see Eq. (18.26)], the first order energy shifts are the eigenvalues of the matrix of the perturbing Hamiltonian with respect to the degenerate states of the unperturbed system. In the present case, we have a $(2\ell + 1) \times (2\ell + 1)$ matrix indexed by m and m' ,

$$\langle n\ell m | eFz | n\ell m' \rangle. \quad (19.14)$$

Notice that n and ℓ are the same on both sides of these matrix elements, because these indices label the unperturbed, degenerate level. Only the index m is allowed to be different on the two sides, because this index labels the basis kets lying in the unperturbed eigenspace.

But we need not do any work to find the eigenvalues of this matrix, because all the matrix elements (19.14) vanish, again by parity. This is because the parity of a central force eigenstate $|n\ell m\rangle$ is $(-1)^\ell$, which is the same on both sides of the matrix elements (19.14). In fact, we see that there will be no linear Stark effect, and no permanent electric dipole moment, in any state of any atom, molecule or nucleus, degenerate or otherwise, unless that state involves a degeneracy between eigenstates of opposite parity. When a Hamiltonian commutes with parity, as we assume, the two subspaces of the Hilbert space corresponding to states of opposite parity (the two eigenspaces of the parity operator) are not coupled by the Hamiltonian, and the eigenvalues of the Hamiltonian operator in one subspace are effectively independent of the eigenvalues in the other subspace. This means that it would take some very unlikely accident, or some systematic symmetry which goes beyond parity, to cause any two energy levels in the two subspaces to coincide exactly. For most systems, such accidents do not happen, although it is possible for two states of opposite parity to have energies which are very close.

In the case of central force problems, since the parity is $(-1)^\ell$, we need a degeneracy between different ℓ values to have a degeneracy between states of opposite parity. Such degeneracy never occurs in the real world, with the one exception of the excited states of hydrogen, where the energy levels E_n are independent of ℓ . Actually, even in hydrogen, the degeneracy between different ℓ values is only an approximation, and does not hold in the real world. The hydrogen energy levels (19.6), which are n^2 -fold degenerate ($2n^2$ if we include the spin), are split and shifted by relativistic effects and the coupling of the electron to the electromagnetic field (the Lamb shift). Relativistic effects alone do not lift the ℓ -degeneracy, that is, this degeneracy persists in the Dirac equation, but the Lamb shift does, so we have to say that in the real world, even in hydrogen, there are no degeneracies between states of opposite parity. In this sense, the linear Stark effect never exists, and no

system has a permanent electric dipole moment. Such a statement is strictly correct for sufficiently weak electric fields.

If, however, we have a system with a near degeneracy between states of opposite parity (which holds for the excited states of hydrogen because the Lamb shift is small), then electric fields which are sufficiently strong will overwhelm the splitting, and cause a mixing of states of opposite parity. Recall that we assumed such strong fields when we neglected spin in our atomic Hamiltonian. Therefore, for sufficiently strong electric fields, we can say that certain systems do exhibit a linear Stark effect, and do behave as if they possess a permanent electric dipole moment. This applies to the excited states of hydrogen, as well as other systems such as polar molecules like HCl, for which rotational states of opposite parity are mixed by reasonably strong electric fields. To fully understand the situation with molecules requires, however, some knowledge of the Born-Oppenheimer approximation.

Let us now analyze the excited states of hydrogen in first-order, degenerate perturbation theory. The shifts in the energy level E_n are given by the eigenvalues of the $n^2 \times n^2$ matrix, indexed by (ℓm) and $(\ell' m')$, with matrix elements

$$\langle n\ell m | eFz | n\ell' m' \rangle. \quad (19.15)$$

Notice the indices which are primed and those which are not. This is potentially a large matrix, but many of the matrix elements vanish because of various symmetry considerations. The ℓ -selection rule, which follows from the Wigner-Eckart theorem and parity, is the same as in the theory of dipole transitions, namely, $\Delta\ell = \pm 1$ (the Wigner-Eckart theorem would allow $\Delta\ell = 0$, but this is excluded by parity). There is also a selection rule on the magnetic quantum number, because the operator z is the $q = 0$ component of a $k = 1$ irreducible tensor operator [see Eq. (15.26)], so the matrix element vanishes unless $m = m'$.

Consider, for example, the case $n = 2$. The four degenerate states include the $2s$ level, with eigenstate $|n\ell m\rangle = |200\rangle$, and the $2p$ level, with eigenstates $|21m\rangle$ for $m = 0, \pm 1$. According to the selection rules, only the states $|200\rangle$ and $|210\rangle$ are connected by the perturbation. Therefore of the 16 matrix elements in the 4×4 matrix, the only nonvanishing ones are

$$\langle 200 | eFz | 210 \rangle = -W \quad (19.16)$$

and its complex conjugate. This matrix element is easily evaluated by resorting to the hydrogen radial wave functions. The result is real and negative, so that W defined above is positive; we find

$$W = 3eFa_0. \quad (19.17)$$

The energy W is of the order of the energy needed to shift the electron from one side of the atom to the other in the external field. The 2×2 matrix connecting the two states $|200\rangle$ and $|210\rangle$ is

$$\begin{pmatrix} 0 & -W \\ -W & 0 \end{pmatrix}, \quad (19.18)$$

and its eigenvalues are the first order energy shifts in the $n = 2$ level,

$$\Delta E_2^{(1)} = \pm W. \quad (19.19)$$

In addition, the two states $|211\rangle$ and $|21, -1\rangle$ do not shift their energies at first order, so the other two eigenvalues of the matrix (19.15) are $\Delta E_2^{(1)} = 0, 0$.

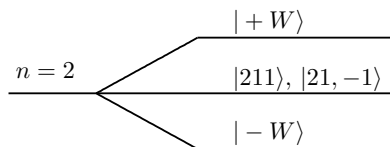


Fig. 19.2. The Stark effect splits the $n = 2$ level of hydrogen into three levels, of which one is two-fold degenerate.

The Stark effect in the $n = 2$ level of hydrogen is illustrated in Fig. 19.2. The 4-fold degeneracy of the unperturbed system is partially lifted, but there remains a 2-fold degeneracy in the states $|211\rangle$ and $|21, -1\rangle$. The perturbation calculation above only reveals this degeneracy through first order, but in fact it holds to all orders. To see this, we note that both L_z and time reversal Θ are exact symmetries of the fully perturbed Hamiltonian, $H = H_0 + H_1$. Since $[L_z, H] = 0$ the exact eigenstates of H can be chosen to be also eigenstates of L_z . Denote these by $|\alpha m\rangle$, where α represents any additional quantum numbers besides the magnetic quantum number m needed to specify an energy eigenstate. We write $H|\alpha m\rangle = E_{\alpha m}|\alpha m\rangle$ and $L_z|\alpha m\rangle = m\hbar|\alpha m\rangle$, so that state $|\alpha m\rangle$ has energy $E_{\alpha m}$. (Note that in a central force problem, the energies are independent of m , but the Stark potential, including the perturbation, is not a central force potential.) Consider now the state $\Theta|\alpha m\rangle$. It is easy to show that this state is an eigenstate of the Hamiltonian with energy $E_{\alpha m}$, since $[\Theta, H] = 0$ and since

$$H(\Theta|\alpha m\rangle) = \Theta H|\alpha m\rangle = E_{\alpha m}(\Theta|\alpha m\rangle). \quad (19.20)$$

However, in view of the conjugation relation (17.9), we also have

$$L_z(\Theta|\alpha m\rangle) = -\Theta L_z|\alpha m\rangle = -m\hbar(\Theta|\alpha m\rangle). \quad (19.21)$$

Thus, $\Theta|\alpha m\rangle$, which has the same energy as $|\alpha m\rangle$, must be a linear combination (over α) of the states $|\alpha, -m\rangle$. If $m \neq 0$, this means $\Theta|\alpha m\rangle$ is linearly independent of $|\alpha m\rangle$, and hence the energy $E_{\alpha m}$ is at least 2-fold degenerate. More generally, one can show that all states with $m \neq 0$ have a degeneracy which is even (the energy depends only on $|m|$). The only energy levels which can be nondegenerate are those with $m = 0$. These conclusions are exactly what we see in Fig. 19.2.

Do not confuse this argument with Kramer’s degeneracy, which applies whenever we have a system with an odd number of fermions. In the present calculation, we are ignoring the spin of the electrons, treating them as if they were spinless particles, so Kramer’s degeneracy does not apply.

The same argument applies to any system in which the Hamiltonian commutes with both L_z and Θ . For example, in the theory of the H_2^+ molecule, we are interested in the motion of an electron in the field of two protons. If we imagine the protons pinned down at locations $z = \pm a/2$ on the z -axis, then the Hamiltonian commutes with both L_z and Θ . Then by the previous argument, all states with $m \neq 0$ are at least doublets. In reality, of course, the protons are not pinned down, but rather the molecule is free to vibrate and rotate like a dumbbell. When these effects are included, it is found that the $\pm m$ doublets become split. This is called “ Λ -doubling,” since Λ (not m) is the standard notation for the magnetic quantum number of the electrons about the axis of a diatomic molecule.

To return to the Stark effect in the $n = 2$ levels of hydrogen, we can also work out the perturbed eigenstates. These are linear combinations of the unperturbed eigenstates, with coefficients given by the eigenvectors of the matrix (19.18). Explicitly, we have

$$\begin{aligned} | + W \rangle &= \frac{1}{\sqrt{2}}(|200\rangle - |210\rangle), \\ | - W \rangle &= \frac{1}{\sqrt{2}}(|200\rangle + |210\rangle). \end{aligned} \tag{19.22}$$

The coefficients in these linear combinations are the same as the coefficients c_α in Eq. (18.23). In the language of Notes 18, we are determining the projection of the exact eigenstates onto the unperturbed eigenspace. This is zeroth order part of the exact eigenstates, since the part orthogonal to the unperturbed eigenspace is small. Notice that even though the perturbation is small, it has caused large (order unity) changes in the eigenkets.

Notice also that the perturbed eigenkets are mixtures with equal probabilities of states of different parity. The phases are different for the two states $|\pm W\rangle$, which causes the charge distribution to be shifted either above or below the origin on the z -axis. The energy

of the state is either raised or lowered compared to the unperturbed energy, depending on whether the charge distribution has been moved with or against the external field.

There is some interesting physics involving radiative transitions and the Stark effect on the $n = 2$ levels of hydrogen. In the absence of an external field, the $2p$ level of hydrogen has a lifetime on the order of 10^{-9} seconds, before the atom emits a photon and drops into the $1s$ state. But the $2s$ level is metastable, and decays much more slowly, mainly via two photon emission, in about 10^{-1} seconds. This makes it easy to create a population of mainly $2s$ and $1s$ states of hydrogen, since if a population of hydrogen atoms is knocked into mixture of excited states, perhaps by collisions with an electron beam, then after a short time everything will have decayed into either the $1s$ state or the metastable $2s$ state. Now the $2s$ state is a linear combination of the states $|\pm W\rangle$,

$$|200\rangle = \frac{1}{\sqrt{2}}(|+W\rangle + |-W\rangle), \quad (19.23)$$

even in the absence of an external field. But if an atom is in the $2s$ state at $t = 0$, at which time an external field is turned on, then the two eigenstates $|\pm W\rangle$ have different energies and evolve with different time-dependent phases, $e^{-iEt/\hbar}$. If there were no radiative transitions, then the state of the system would oscillate between the states $|200\rangle$ and $|210\rangle$ with a frequency determined by the energy difference, $2W$. But because of the radiative transitions, the state $|210\rangle$ drops down into the ground state in about 10^{-9} seconds. The effect is to rapidly depopulate the $2s$ state, and to cause the emission of a burst of photons. This phenomenon is called *quenching*.

Let us return to the ground state of hydrogen. Although the first order Stark energy shift in this state vanishes, the first order shift in the wave function is nonzero. We see this from Eq. (18.22), which in the present notation is

$$|\psi\rangle = |100\rangle + \sum_{(nlm) \neq (100)} |nlm\rangle \frac{\langle nlm|eFz|100\rangle}{E_1 - E_n}. \quad (19.24)$$

Here $|\psi\rangle$ is the perturbed ground state. This state has a nonzero electric dipole moment, unlike the unperturbed ground state. For if we compute the expectation value of the dipole operator $\mathbf{d} = -e\mathbf{r}$ and carry the answer to first order in the perturbation, we find

$$\langle \mathbf{d} \rangle = \langle \psi | \mathbf{d} | \psi \rangle = \alpha \mathbf{F}, \quad (19.25)$$

where the *polarizability* α is given by

$$\alpha = -2e^2 \sum_{(nlm) \neq (100)} \frac{\langle 100|z|nlm\rangle \langle nlm|z|100\rangle}{E_1 - E_n}. \quad (19.26)$$

The x - and y -components vanish in Eq. (19.25), and α is positive in Eq. (19.26) because the energy denominator is negative. The polarizability α is a scalar in this problem, but more generally it will be a tensor giving the linear relationship between the induced dipole moment and the electric field,

$$d_i = \sum_j \alpha_{ij} F_j. \quad (19.27)$$

Given the polarizability of a single atom, it is straightforward to compute the dielectric constant of a gas of the atoms, although for hydrogen under normal circumstances it is unrealistic to speak of a gas of atoms (as opposed to molecules). This is an example of how electric susceptibilities can be computed from first principles.

Since the first order energy shift in the ground state vanishes, it is of interest to compute the second order shift. We invoke Eq. (18.21) with necessary changes of notation, to write

$$\Delta E_{\text{gnd}}^{(2)} = \sum_{(n\ell m) \neq (100)} \frac{\langle 100 | eFz | n\ell m \rangle \langle n\ell m | eFz | 100 \rangle}{E_1 - E_n} = -\frac{1}{2} \alpha F^2. \quad (19.28)$$

We see that the second order energy shift can be expressed in terms of the polarizability. This energy can also be written,

$$\Delta E_{\text{gnd}}^{(2)} = -\frac{1}{2} \langle \mathbf{d} \rangle \cdot \mathbf{F}. \quad (19.29)$$

The presence of the factor $\frac{1}{2}$ in this formula may be puzzling, since we are accustomed to thinking of the energy of a dipole in a field as $-\mathbf{d} \cdot \mathbf{F}$. The reason for this factor is that the dipole moment is induced by the external field, and is itself proportional to \mathbf{F} ; the energy (19.29) is the work done on the atom by the external field as it builds up from zero to its maximum value.

It is of interest to evaluate the sum (19.26), to obtain a closed form expression for the polarizability α . This sum contains an infinite number of terms, and, in fact, it is more complicated than it appears, because the continuum states must also be included (there is an integral over the continuum states as well as a sum over the discrete, bound states). There are various exact methods of evaluating this sum, but we will content ourselves with an estimate. We begin with the fact that the energy levels E_n increase with n , so that

$$E_n - E_1 > E_2 - E_1 = \frac{3}{8} \frac{e^2}{a_0}. \quad (19.30)$$

But this implies that

$$\alpha < \frac{2e^2}{E_2 - E_1} \sum_{n\ell m} \langle 100 | z | n\ell m \rangle \langle n\ell m | z | 100 \rangle. \quad (19.31)$$

We excluded the term $(n\ell m) = (100)$ in Eq. (19.26), but we can restore it in Eq. (19.31) after taking out the constant denominator, since this term vanishes anyway. The result contains a resolution of the identity, so that the sum in Eq. (19.31) becomes the matrix element,

$$\langle 100|z^2|100\rangle = a_0^2. \quad (19.32)$$

This gives the estimate

$$\alpha < \frac{16}{3}a_0^3. \quad (19.33)$$

An exact treatment of the sum (19.26) gives the result,

$$\alpha = \frac{9}{2}a_0^3, \quad (19.34)$$

so the exact expression for the second order energy shift is

$$\Delta E_{\text{gnd}}^{(2)} = -\frac{9}{4}F^2a_0^3. \quad (19.35)$$

This energy shift is of the order of the energy of the external field contained in the volume of the atom.