

Lecture 7

Time-Dependent Perturbation Theory Interaction of Atoms with E. M. Radiation

17.1 Introduction

So far we have concentrated on systems for which we could find exactly the eigenvalues and eigenfunctions of the Hamiltonian, like e.g. the harmonic oscillator, the quantum rotator, or the hydrogen atom.

However the vast majority of systems in Nature cannot be solved exactly, and we need to develop appropriate tools to deal with them.

Perturbation theory is extremely successful in dealing with those cases that can be modelled as a “small deformation” of a system that we can solve exactly.

Let us translate the above statement into a precise mathematical framework. We are going to consider systems that have an Hamiltonian:

$$\hat{H} = \hat{H}_0 + V, \quad (17.1)$$

where \hat{H}_0 is the Hamiltonian of the unperturbed system, ϵ is a small parameter, and V is the potential describing the perturbation. We shall assume that the perturbation V is independent of time.

Let us also assume that we can solve the time-independent Schrödinger equation for \hat{H}_0 , i.e. that we know its eigenvalues and eigenfunctions:

$$\hat{H}_0 \psi(n)(x) = E(n) \psi(n)(x). \quad (17.2)$$

For simplicity we start by considering the case where all the unperturbed levels $E^{(n)}$ are not degenerate.

17.2 Perturbative solution

Let us discuss the solution of the time-independent Schrödinger equation for the full Hamiltonian H . The eigenvalue equation reads:

$$H\psi(x) = E\psi(x). \quad (17.3)$$

Since ϵ is a small parameter, we shall expand the solution of Eq. (17.3) as a Taylor series in ϵ :

$$\psi(x) = \psi_0(x) + \epsilon\psi_1(x) + \epsilon^2\psi_2(x) + \dots, \quad (17.4)$$

$$E = E_0 + \epsilon E_1 + \epsilon^2 E_2 + \dots. \quad (17.5)$$

Plugging Eqs. (17.4) and (17.5) into Eq. (17.3), we obtain:

$$H_0 + \epsilon V \psi_0(x) + \epsilon\psi_1(x) + \epsilon^2\psi_2(x) + \dots =$$

$$E_0 + \epsilon E_1 + \epsilon^2 E_2 + \dots \psi_0(x) + \epsilon\psi_1(x) + \epsilon^2\psi_2(x) + \dots \quad (17.6)$$

We can now solve Eq. (17.6) order by order in ϵ .

17.2. PERTURBATIVE SOLUTION

Order ϵ^0 At order ϵ^0 we find:

$$H_0\psi_0 - E_0\psi_0 = 0, \quad (17.7)$$

and therefore ψ_0 has to be one of the unperturbed eigenfunctions $\psi^{(n)}$, and E_0 must be the corresponding unperturbed eigenvalue $E^{(n)}$. Since

we assumed that the unperturbed levels are nondegenerate the choice of $\psi^{(n)}$ is unique.

Order 1 At order we have:

$$\hat{H}_0 - E_0\psi_1 + \hat{V} - E_1\psi_0 = 0. \quad (17.8)$$

Taking the scalar product of Eq. (17.8) with ψ_0 yields:

$$\psi_0|\hat{H}_0|\psi_1 + \psi_0|\hat{V}|\psi_0 = E_0\psi_0|\psi_1 + E_1\psi_0|\psi_0. \quad (17.9)$$

Since \hat{H}_0 is Hermitean, the first term on the LHS of Eq. (17.9) cancels with the first term on the RHS, and we are left with:

$$E_1 = \frac{\langle \psi_0|\hat{V}|\psi_0 \rangle}{\langle \psi_0|\psi_0 \rangle}. \quad (17.10)$$

To first order in the perturbation parameter, the shift of the n -th energy eigenvalue is given by Eq. (17.10). Hence the eigenvalue of the Hamiltonian is:

$$E = E^{(n)} + \frac{\psi^{(n)}|\hat{V}|\psi^{(n)}}{\psi^{(n)}|\psi^{(n)}} + O(\epsilon^2). \quad (17.11)$$

This is a very useful result, since it allows us to compute the perturbed energy levels starting from the unperturbed ones.

Let us now consider the scalar product of Eq. (17.8) with $\psi^{(m)}$, for $\psi^{(m)} \neq \psi_0$:

$$\psi^{(m)}|\hat{H}_0|\psi_1 + \psi^{(m)}|\hat{V}|\psi_0 = E_0\psi^{(m)}|\psi_1 + E_1\psi^{(m)}|\psi_0. \quad (17.12)$$

Using the fact that:

$$\psi^{(m)}|\psi_0 = 0, \quad (17.13)$$

we obtain:

$$\langle \psi^{(m)} | \psi_1 \rangle = \frac{\langle \psi^{(m)} | \hat{V} | \psi_0 \rangle}{E_0 - E^{(m)}}. \quad (17.14)$$

Hence at first order in ϵ we have:

$$\psi(x) = \psi^{(n)}(x) + \epsilon \sum_{m \neq n} \frac{\langle \psi^{(m)} | \hat{V} | \psi^{(n)} \rangle}{E^{(n)} - E^{(m)}} \psi^{(m)}(x) + \mathcal{O}(\epsilon^2). \quad (17.15)$$

Using Dirac's notation, we can rewrite the solution above as:

$$|\psi\rangle = |\psi^{(n)}\rangle + \epsilon \sum_{m \neq n} \frac{\langle \psi^{(m)} | \hat{V} | \psi^{(n)} \rangle}{E^{(n)} - E^{(m)}} |\psi^{(m)}\rangle + \mathcal{O}(\epsilon^2). \quad (17.16)$$

Note that to first order in ϵ the solution in Eq. (17.16) is already

$$\begin{aligned} \langle \psi | \psi \rangle &= \langle \psi^{(n)} | \psi^{(n)} \rangle + \epsilon \sum_{m \neq n} \left[\frac{\langle \psi^{(m)} | \hat{V} | \psi^{(n)} \rangle}{E^{(n)} - E^{(m)}} \langle \psi^{(n)} | \psi^{(m)} \rangle + \text{c.c.} \right] + \mathcal{O}(\epsilon^2) \\ &= 1 + \mathcal{O}(\epsilon^2). \end{aligned}$$

normalized:

$$) (17.17)$$

$$(17.18)$$

Example A particle moves in the 1-dimensional potential

$$V(x) = \infty, \quad |x| > a, \quad V(x) = V_0 \cos(\pi x/2a), \quad |x| \leq a$$

Calculate the ground-state energy to first order in perturbation theory.

Here we take the unperturbed Hamiltonian, H_0 , to be that of the infinite square well, for which we already know the eigenvalues and eigenfunctions:

$$E(n) = \frac{\pi^2 \hbar^2}{8ma^2} n^2, \quad \psi(n) = \sqrt{\frac{2}{a}} \begin{cases} \cos(n\pi x/2a); & n \text{ even} \\ \sin(n\pi x/2a); & n \text{ odd} \end{cases}$$

The perturbation \hat{H} is $V_0 \cos(\pi x/2a)$, which is small provided V_0

$E^{(2)} - E^{(1)}$. To first order, then,

$$\Delta E \equiv E_1 = H'_{11} = \int_{-\infty}^{\infty} u^{(1)} \hat{H}' u^{(1)} dx = \frac{V_0}{a} \int_{-a}^a \cos^3 \frac{\pi x}{2a} dx$$

Evaluating the integral is straightforward and yields the result

$$\Delta E = \frac{8V_0}{3\pi} = 0.85 V_0$$

Iterative solution At order L the eigenvalue equation yields:

L

$$H_0 \psi_L - E_0 \psi_L + V \psi_{L-1} - E_K \psi_{L-K} = 0. \quad (17.19)$$

$K=2$

Taking the same scalar products described above, we find:

$$E_L = \langle \psi_0 | V | \psi_{L-1} \rangle, \quad (17.20)$$

17.3. DEGENERATE LEVELS

which yields the correction of order L to the unperturbed energy level. Following the computation above we also obtain:

$$\langle \psi^{(m)} | \psi_L \rangle = \frac{\langle \psi^{(m)} | V | \psi_{L-1} \rangle}{E^{(n)} - E^{(m)}} - \frac{1}{E^{(n)} - E^{(m)}} \sum_{K=1}^{L-1} E_K \langle \psi^{(m)} | \psi_{L-K} \rangle. \quad (17.21)$$

Using Eq. (17.21) for $L = 2$ we find the second-order correction to the n -th energy level:

$$E_2 = \langle \psi_0 | \hat{V} | \psi_1 \rangle = \sum_{m \neq n} \frac{\langle \psi^{(n)} | \hat{V} | \psi^{(m)} \rangle \langle \psi^{(m)} | \hat{V} | \psi^{(n)} \rangle}{E^{(n)} - E^{(m)}}. \quad (17.22)$$

17.3 Degenerate levels

Equation (17.15) shows that the correction to the energy eigenfunctions at first order in perturbation theory is small only if

$$\frac{\langle \psi^{(m)} | \hat{V} | \psi^{(n)} \rangle}{E^{(n)} - E^{(m)}} \simeq 1. \quad (17.23)$$

If the energy splitting between the unperturbed levels is small compared to the matrix element in the numerator, then the perturbation becomes large, and the approximation breaks down. In particular, if there are degenerate levels, the denominator is singular, and the solution is not applicable.

Let us see how we can deal with a g_0 -fold degenerate level of the unperturbed Hamiltonian. We shall denote P the projector onto such level, and Q the projector orthogonal to this level. The first-order equation:

$$H_0 \psi_1 + V \psi_0 - E_1 \psi_0 = 0 \quad (17.24)$$

can be projected using P onto the space spanned by the degenerate states:

$$P V \psi_0 - E_1 \psi_0 = 0. \quad (17.25)$$

Choosing a basis for the space of degenerate levels, we can write ψ_0 as:

$$\psi_0 = \sum_{i=1}^{g_0} c_i \varphi_i, \quad (17.26)$$

$$\psi_0 = \sum_{i=1}^{g_0} c_i \varphi_i,$$

$$i=1$$

and then rewrite Eq. (17.25):

$$\sum_j \langle \varphi_i | V | \varphi_j \rangle c_j = E_1 c_i, \quad (17.27)$$

i.e. E_1 is an eigenvalue of the matrix $V_{ij} = \langle \varphi_i | V | \varphi_j \rangle$. This equation has g_0 roots (not necessarily distinct), and generalizes Eq. (17.10) to the case of degenerate levels. If the eigenvalues are indeed all distinct, then the degeneracy is completely lifted. If some of the eigenvalues are equal, the degeneracy is only partially lifted.

Example A well-known example of degenerate perturbation theory is the Stark effect, i.e. the separation of levels in the H atom due to the presence of an electric field. Let us consider the $n = 2$ level, which has a 4-fold degeneracy:

$$|2s\rangle, |2p, 0\rangle, |2p, +1\rangle, |2p, -1\rangle. \quad (17.28)$$

The electric field is chosen in the z -direction, hence the perturbation can be written as:

$$V = -ezE, \quad (17.29)$$

where E is the magnitude of the electric field.

We need to compute the matrix V_{ij} in the subspace of the unperturbed states of the H atom with $n = 2$. This is a 4×4 Hermitean matrix.

Note that the perturbation V is odd under parity, and therefore it has non-vanishing matrix elements only between states of opposite parity. Since the eigenstates of the H atom are eigenstates of L^2 and L_z , we find that only the matrix elements between s and p states can be different from zero.

Moreover, V commutes with L_z and therefore only matrix elements between states with the same value of L_z are different from zero.

So we have proved that the only non-vanishing matrix elements are $\langle 2s|V|2p, 0\rangle$ and its Hermitean conjugate. Hence the matrix V is given by:

$$\begin{pmatrix} 0 & 3e\mathcal{E}a_0 & 0 & 0 \\ 3e\mathcal{E}a_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad (17.30)$$

where a_0 is the Bohr radius. We see that the external field only removes the degeneracy between the $|2s$, and the $|2p,0$ states; the states $|2p,\pm 1$ are left unchanged. The two other levels are split:

$$E = E_2 \pm 3ea_0E. \quad (17.31)$$

17.4 Applications

There are numerous applications of perturbation theory, which has proven to be a very effective tool to gain quantitative information on the dynamics of a system whenever a small expansion parameter can be identified.

Here we discuss briefly two examples.

17.4. APPLICATIONS

17.4.1 Ground state of Helium

We can now attempt to incorporate the effect of the inter-electron Coulomb repulsion by treating it as a perturbation. We write the Hamiltonian as

$$\boxed{H = H_0} + \boxed{H'}$$

where

$$H_0 = H_1 + H_2 \quad \text{and} \quad \hat{H}' = \frac{e^2}{4\pi\epsilon_0|r_1 - r_2|}$$

The ground state wavefunction that we wrote down earlier is an eigenfunction of the unperturbed Hamiltonian, H_0 ;

$$\Psi(\text{ground state}) = u_{100}(r_1)u_{100}(r_2)\chi_{0,0}.$$

To compute the first order correction to the ground state energy, we have to evaluate the expectation value of the perturbation, H' , with respect to this wavefunction;

$$\Delta E_1 = \frac{e^2}{4\pi\epsilon_0} \int u_{100}^*(\underline{r}_1) u_{100}^*(\underline{r}_2) \chi_{0,0}^* \frac{1}{r_{12}} u_{100}(\underline{r}_1) u_{100}(\underline{r}_2) \chi_{0,0} d\tau_1 d\tau_2$$

The scalar product of $\chi_{0,0}$ with its conjugate = 1, since it is normalised. Putting in the explicit form of the hydrogenic wavefunction from Lecture 10

$$u_{100}(\underline{r}) = \frac{1}{\sqrt{\pi}} (Z/a_0)^{3/2} \exp(-Zr/a_0)$$

thus yields the expression

$$\Delta E_1 = \frac{e^2}{4\pi\epsilon_0} \frac{Z^3}{\pi a_0^3} \frac{1}{r_{12}} \int \exp\{-2Z(r_1 + r_2)/a_0\} d\tau_1 d\tau_2$$

Amazingly, this integral can be evaluated analytically. See, for example, Bransden and Joachain, *Introduction to Quantum Mechanics*, pp 465-466. The result is

$$\Delta E_1 = \frac{5}{4} Z Ry = \frac{5}{2} Ry = 34 eV$$

giving for the first-order estimate of the ground state energy

$$E_1 = -108.8 + 34 eV = -74.8 eV = -5.5 Ry$$

to be compared with the experimentally-measured value of $-78.957 eV$.

17.4.2 Spin-orbit effects in hydrogenic atoms

Classically, an electron of mass M and charge $-e$ moving in an orbit with angular momentum

\underline{L} would have a magnetic moment

$$\underline{\mu} = -\frac{e}{2M} \underline{L}$$

suggesting that in the quantum case,

$$\hat{\mu} = -\frac{e}{2M} \hat{L} \quad \text{and} \quad \mu_z = -\frac{e}{2M} \hat{L}_z$$

The eigenvalues of $\hat{\mu}_z$ are thus given by

$$-\frac{e\hbar}{2M} m_\ell \equiv -\mu_B m_\ell,$$

where the quantity μ_B is known as the *Bohr magneton*.

Similarly, there is a magnetic moment associated with the intrinsic spin of the electron;

$$\hat{\mu}_z = -\frac{g_s e}{2M} \hat{S}_z$$

where the constant, g_s , cannot be determined from classical arguments, but is predicted to be 2 by relativistic quantum theory and is found experimentally to be very close to 2.

The interaction between the orbital and spin magnetic moments of the electron introduces an extra term into the Hamiltonian of the form

$$H_{S-O} = f(r) \hat{L} \cdot \hat{S}$$

where

$$f(r) = \frac{1}{2} \frac{\hbar^2}{2M c r} \quad (r)$$

We can attempt to treat this extra term by the methods of perturbation theory, by taking the unperturbed Hamiltonian to be

$$\hat{H}_0 = \frac{\hat{p}^2}{2M} + V(r) = \frac{\hat{p}^2}{2M} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

Cautionary Note In our derivation of the first-order formula for the shift in energy induced by a perturbation, we assumed that there were no degeneracies in the energy eigenvalue spectrum and noted that the method could break down in the presence of degeneracies.

- In general, when considering the effects of a perturbation on a degenerate level, *it is necessary to use degenerate state perturbation theory*, which we briefly discussed above.

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- There are, however, important exceptions to this rule. In particular, *if the perturbation H' , is diagonal with respect to the degenerate states, the non-degenerate theory can be used to compute the energy shifts.*

In the case of the spin-orbit interaction in the hydrogenic atom, we know that the degeneracy of a level with given n and l is $(2l + 1) \times 2$, since, for a given l , there are $(2l + 1)$ possible values of m and 2 possible values of m_s .

However, if we choose to work with states of the coupled basis $|n, j, m_j, s\rangle$, rather than with the states of the uncoupled basis $|n, l, m, s, m_s\rangle$, we can use non-degenerate theory. Firstly, we note that we can rewrite the spin-orbit term as follows:

$$\hat{H}_{S-O} = f(r) \hat{\underline{L}} \cdot \hat{\underline{S}} = \frac{1}{2} f(r) \{ \hat{J}^2 - \hat{L}^2 - \hat{S}^2 \}$$

using the fact that $\hat{J}^2 \equiv (\hat{\underline{L}} + \hat{\underline{S}})^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{\underline{L}} \cdot \hat{\underline{S}}$.

Noting that

$\{J^2 - L^2 - S^2\}|n, j, m_j, s\rangle = \{j(j + 1) - \ell(\ell + 1) - s(s + 1)\} \hbar^2 |n, j, m_j, s\rangle$ we see that the expectation value of H' in the unperturbed basis is

$$\langle n, j, m_j, \ell, s | \hat{H}_{S-O} | n, j, m_j, \ell, s \rangle = \frac{1}{2} \{j(j + 1) - \ell(\ell + 1) - s(s + 1)\} \hbar^2 \langle f(r) \rangle$$

Since $f(r)$ is independent of the angular variables θ, φ and of the spin, the expectation value of $f(r)$ may be written

$$\langle f(r) \rangle = \frac{Ze^2}{8\pi\epsilon_0 M^2 c^2} \int_0^\infty \frac{1}{r^3} |R_{n\ell}(r)|^2 r^2 dr$$

The integral can be evaluated exactly using the hydrogenic radial functions and gives:

$$\left\langle \frac{1}{r^3} \right\rangle_{n\ell} = \frac{Z^3}{a_0^3} \frac{1}{n^3 \ell (\ell + \frac{1}{2}) (\ell + 1)}$$

Now $s = \frac{1}{2}$ for an electron, so that j can have two values for a given ℓ , namely, $j = (\ell + \frac{1}{2})$ and $j = (\ell - \frac{1}{2})$, except in the case $\ell = 0$, which means that a state of given n and ℓ separates into a doublet when the spin-orbit interaction is present.

Term Notation There is yet another piece of notation used widely in the literature, the so-called *term notation*. The states that arise in coupling orbital angular momentum ℓ and spin s to give total angular momentum j are denoted:

$(2S+1)L_J$

where L denotes the letter corresponding to the ℓ value in the usual way, and the factor $(2S + 1)$ is the spin multiplicity i.e. the number of allowed values of m_s .