## 2 Review: Time-Independent Non-degenerate Perturbation Theory

There's nothing new in this section, its simply an alternative derivation to the one you saw last year in Junior Honours. If you prefered that derivation, feel free to read over those notes, the results are the same!

### 2.1 Small changes to the Hamiltonian

There are very few problems in quantum mechanics which can be solved exactly. However, we are often interested in the effect of a small change to a system, and in such cases we can proceed by assuming that this causes only a small change in the eigenstates. *Perturbation theory* provides a method for finding approximate energy eigenvalues and eigenfunctions for a system whose Hamiltonian is of the form

$$\hat{H} = \hat{H}_0 + \hat{V}$$

where $\hat{H}_0$ is the 'main bit' of the Hamiltonian of an exactly solvable system, for which we know the eigenvalues, $E_n$, and eigenfunctions, $|n\rangle$, and $\hat{V}$ is a *small*, time-independent perturbation. $\hat{H}$, $\hat{H}_0$ and $\hat{V}$ are Hermitean operators. Using perturbation theory, we can get approximate solutions for $\hat{H}$ using as basis functions eigenstates of the similar, exactly solvable system $\hat{H}_0$.

Assuming that $\hat{H}$ and $\hat{H}_0$ possess discrete, non-degenerate eigenvalues only, we write

$$\hat{H}_0 \, |n_i\rangle = E_i \, |n_i\rangle$$

in Dirac notation. The states $|n_i\rangle$ are orthonormal. WLOG, consider a state $i = 0$: the effect of the perturbation will be to modify the state and its corresponding energy slightly; The eigenstate $|n_0\rangle$ will become $|\phi_0\rangle$ and $E_0$ will shift to $E_0 + \Delta E_0$, where

$$\hat{H} \, |\phi_0\rangle = E_0 + \Delta E_0 \, |\phi_0\rangle$$

WLOG, expanding $|\phi_0\rangle$ in the basis set $|n_i\rangle$ with coefficients $c_{i0}$ and premultiplying by $\langle n_0|$

$$\langle n_0|(\hat{H}_0 + \hat{V}) \sum_{i=0,\infty} c_{i0} \, |n_i\rangle = (E_0 + \Delta E_0) \, \langle n_0| \sum_{i=0,\infty} c_{i0} \, |n_i\rangle$$

Which after a little algebra and cancellation yields the exact result:

$$\Delta E_0 = \langle n_0|\hat{V} \, |n_0\rangle + \sum_{i=1,\infty} (c_{i0}/c_{00}) \langle n_0|\hat{V} \, |n_i\rangle \tag{1}$$

Similarly, expanding $|\phi_0\rangle$ in the basis set $|n_i\rangle$ and premultiplying by another state $\langle n_k|$

$$\langle n_k|(\hat{H}_0 + \hat{V}) \sum_{i=0,\infty} c_{i0}|n_i\rangle = (E_0 + \Delta E_0) \, \langle n_k| \sum_{i=0,\infty} c_{i0} \, |n_i\rangle$$

leading to $|\phi_0 \, \rangle$ having a component of $|n_k\rangle$

$$c_{k0}(E_0 + \Delta E_0 - E_k) = \sum_{i=0,\infty} c_{i0} \langle n_k|\hat{V} \, |n_i\rangle \tag{2}$$

Note that although we have denoted the unperturbed state as $|n_0\rangle$, it is not necessarily the ground state.

### 2.2 First order energy shifts

In first order perturbation theory, we assume that the change in the wavefunction is small, i.e. $|c_{i0}/c_{00}| \ll 1 \, \forall i$ and neglect the second term in equation 1 which becomes.

$$\Delta E_0 \approx \langle n_0 | \hat{V} | n_0 \rangle \equiv V_{00}$$

which is one of *the most useful results in quantum mechanics*. It tells us how to calculate the change in the $n$th energy eigenvalue, to first order:

> **The shift in energy induced by a perturbation is given to first order by the expectation value of the perturbation with respect to the unperturbed state.**

Thus first order time independent perturbation is equivalent to making the approximation that *the wavefunction does not change*. Loosely, this works because the energy depends on the perturbation to first order, but on wavefunction *squared*.

### 2.3 Mixing of the eigenstates of $\hat{H}_0$

Turning to equation 2, we make the approximation $c_{i0} \ll c_{00} \approx 1 \, \forall i \neq 0$ so that the only significant term in the sum comes from $i = 0$, and also that $\Delta E_0$ is negligible compared to the energy difference between states 0 and $k$:

$$c_{k0} \approx \langle n_k | \hat{V} | n_0 \rangle / (E_0 - E_k) \tag{3}$$

Using these coefficients, we see that the perturbation causes a first-order correction to the energy eigenvector $|n_0\rangle$:

$$|\phi_0\rangle = |n_0\rangle + \sum_{k \neq 0} \frac{\langle n_k | \hat{V} | n_0 \rangle}{(E_0 - E_k)} |n_k\rangle \equiv |n_0\rangle + \sum_{k \neq 0} \frac{V_{k0}}{(E_0 - E_k)} |n_k\rangle$$

Which defines the *matrix element* $V_{ij}$ for $i = k, j = 0$. We speak of the perturbation *mixing the unperturbed eigenfunctions* since the effect is to add to the unperturbed eigenfunction, $|n_0\rangle$, a small amount of each of the other unperturbed eigenfunctions. The denominator suggests that states with similar energies are more strongly mixed, and the "matrix element" determines how the perturbation mixes the states.

Unlike the formula for the energy shift, we are faced in general with evaluating an infinite sum to find the correction to the eigenfunctions.

### 2.4 Higher Orders

It may turn out that the matrix element $V_{00}$ is zero, often due to symmetry. In this case we must consider what happens at second order. Going back to equation 1, and using our expression for mixing and assumption $c_{00} \approx 1$

$$\Delta E_0 = 0 + \sum_{i=1,\infty} \langle n_i | \hat{V} | n_0 \rangle \, \frac{V_{0i}}{(E_0 - E_i)} = \sum_{i=1,\infty} \frac{|V_{i0}|^2}{(E_0 - E_i)}$$

### 2.5 Notes

- The results in 2.2 2.3 and 2.4 are worth memorising: physicists use them without proof.
- Energy shifts are real numbers, but matrix elements may be complex.
- If the perturbation operator commutes with the Hamiltonian, "Off-diagonal" matrix elements ($V_{ij}$, $i \neq j$) are zero. Such perturbations change the energy, but not the wavefunction.
- If the perturbation is turned on and off again, the off-diagonal matrix elements determine whether the quantum state is changed.
- To help with notation, we have derived results for perturbation to a state labelled by 0. This is not necessarily the ground state - the above derivation is general.
- For the first-order changes to the eigenfunction to be small we must have:

$$\langle n_k|\hat{V}\,|n_0\rangle \equiv V_{k0} \ll |(E_0 - E_k)| \qquad \text{for all } k \neq n$$

- Similarly, we require that the level shift be small compared to the level spacing in the unperturbed system:

$$|\Delta E_0| \ll \min|(E_0 - E_k|$$

- These conditions may break down *if there are degeneracies in the unperturbed system.* However, we need only assume that the *particular energy level whose shift we are calculating is non-degenerate* for the preceding analysis to be correct.
- The first order corrected wavefunctions are not fully normalised.
- The second order term always lowers the energy of the ground state.

### 2.6 Example

Consider a simple harmonic oscillator in its ground state, to which we apply a perturbation $\hat{V} = \lambda x^2$. We know the unperturbed wavefunction $|n_0\rangle = [m\omega_0/\pi\hbar]^{\frac{1}{4}} \exp\{-m\omega_0 x^2/2\hbar\}$, so we can evaluate the first order shift in energy according to the perturbation theory:

$$\Delta E_0 = \langle n_0|\lambda x^2|n_0\rangle = \lambda\sqrt{m\omega_0/\pi\hbar}\int x^2 \exp\{-m\omega_0 x^2/\hbar\}dx = \frac{\lambda}{2}\frac{\hbar}{m\omega_0}$$

In this case we know the exact shift, since the perturbation is simply an additional harmonic potential, giving a total $k = m\omega_0^2 + 2\lambda$ and an exact ground state energy of $\frac{1}{2}\hbar\sqrt{\omega_0^2 + 2\lambda/m}$. It is easy to verify that to first order in $\lambda$ these expressions are identical.

To determine the amount of mixing of states, we need to evaluate matrix elements like $\langle n_0|\lambda x^2|n_i\rangle$. We won't evaluate these here, but we will note that for odd $i$ the integral is zero - the symmetric perturbation only mixes in symmetric excited states.

# 3 Dealing with Degeneracy

## 3.1 Time-Independent Degenerate Perturbation Theory

We have seen how we can find approximate solutions for a system whose Hamiltonian is of the form

$$\hat{H} = \hat{H}_0 + \hat{V}$$

When we assumed that $\hat{H}$ and $\hat{H}_0$ possess discrete, non-degenerate eigenvalues only. This led to a mixing of states where

$$|\phi_0\rangle = |n_0\rangle + \sum_{k\neq 0} \frac{V_{k0}}{(E_0 - E_k)} |n_k\rangle$$

Clearly, if $E_0 = E_k$ this diverges. As do the higher order energy shifts (see 2.4). Thus for the degenerate case we cannot associate a particular xperturbed state $|\phi_0\rangle$ with a particular unperturbed state $|n_0\rangle$: we need to take a different approach. In fact, the approximation we make is completely different: we assume that the small perturbation *only mixes those states which are degenerate*. We then solve the problem exactly for that subset of states.

Assume that $\hat{H}_0$ possesses $N$ degenerate eigenstates $|m\rangle$ with eigenvalue $E_{deg}$. It may also possesses non-degenerate eigenstates, which can be treated separately by non-degenerate perturbation theory. We write a perturbed eigenstate $|\phi_j\rangle$ as an linear expansion in the unperturbed degenerate eigenstates only:

$$|\phi_j\rangle = \sum_i |m_i\rangle\langle m_i|\phi_j\rangle = \sum_i c_{ji} |m_i\rangle$$

Where $i$ here runs over degenerate states only. The TISE now becomes:

$$[\hat{H}_0 + \hat{V}] |\phi_j\rangle = [\hat{H}_0 + \hat{V}] \sum_i c_{ni} |m_i\rangle = E_j \sum_i c_{ni} |m_i\rangle$$

but we know that for all degenerate eigenstates $\hat{H}_0|m_i\rangle = E_{deg} |m_i\rangle$. So we obtain:

$$\sum_i c_{ji} \hat{V}|m_i\rangle = (E_j - E_{deg}) \sum_i c_{ji} |m_i\rangle$$

premultiplying by some unperturbed state $\langle m_k|$ gives

$$\sum_i c_{ji} \Big[\langle m_k|\hat{V}|m_i\rangle - \delta_{ik}(E_j - E_{deg})\Big] = 0$$

We can get a similar equation from each unperturbed state $|m_k\rangle$. We thus have an eigenvalue problem: the eigenvector has elements $c_{ji}$ and the eigenvalues are $\Delta E_j = E_j - E_{deg}$. Writing the matrix elements between the $i^{th}$ and $k^{th}$ unperturbed degenerate states as $V_{ik} \equiv \langle m_i|\hat{V}|m_k\rangle$ we recover the determinantal equation:

$$\begin{vmatrix} V_{11} - \Delta E_j & V_{12} & ... & V_{1N} \\ V_{21} & V_{22} - \Delta E_j & ... & V_{2N} \\ ... & ... & ... & ... \\ V_{N1} & V_{N2} & ... & V_{NN} - \Delta E_j \end{vmatrix} = 0$$

The $N$ eigenvalues obtained by solving this equation give the shifts in energy due to the perturbation, and the eigenvectors give the perturbed states $|\phi\rangle$ in the unperturbed, degenerate basis set $|m\rangle$.