

Perturbation theory in atomic physics

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May 13, 2010

These notes are rough and incomplete. They are intended to clarify some points about using degenerate perturbation theory in the study of atomic structure.

Generalities

Recall that in quantum mechanics we cannot simultaneously specify exact values for all physical observables. Rather, we choose our basis for the physical Hilbert space to consist of vectors which are simultaneous eigenvectors of a maximal set of commuting Hermitian operators.

Almost always, we are interested in studying the energy eigenstates of a system. So, given the Hamiltonian \hat{H} , we need to find a set of operators which commute with \hat{H} and each other. The eigenvalues of these operators are then our ‘good quantum numbers’, used to label states.

Degenerate perturbation theory

Suppose our Hamiltonian is a sum of two operators:

$$\hat{H} = \hat{H}^{(0)} + \epsilon \hat{H}^{(1)}$$

where $\epsilon \ll 1$. Suppose further than we have already ‘solved’ the system corresponding to $\hat{H}^{(0)}$. In other words, we have a complete set of eigenvalues/vectors of \hat{H}_0 :

$$\hat{H}^{(0)}|\alpha, i\rangle = E_\alpha^{(0)}|\alpha, i\rangle \quad (1)$$

Here the label i represents extra quantum numbers to distinguish degenerate states. In the B1 course we want only the simplest result from perturbation theory: the eigenvalues of \hat{H} to first order in ϵ . The energy eigenstates will also change; focussing on a single state which has energy $E_\alpha^{(0)}$ in the limit $\epsilon \rightarrow 0$, we expand it in terms of the eigenstates of $\hat{H}^{(0)}$:

$$\begin{aligned} |\alpha, I\rangle &= |\alpha, I\rangle^{(0)} + \epsilon |\alpha, I\rangle^{(1)} + \mathcal{O}(\epsilon^2) \\ &= \sum_i c_{I,i}^{(0)} |\alpha, i\rangle + \epsilon \sum_{i, \beta \neq \alpha} c_{I,\beta,i}^{(1)} |\beta, i\rangle + \mathcal{O}(\epsilon^2) \end{aligned}$$

I represents another set of quantum numbers, labelling the same states as i . The perturbation will generally break the degeneracy, and therefore the corrections to the eigenvalues will depend on I :

$$E_{\alpha,I} = E_\alpha^{(0)} + \epsilon E_{\alpha,I}^{(1)} + \mathcal{O}(\epsilon^2)$$

We can expand the eigenvalue equation $\hat{H}|\alpha, I\rangle = E_{\alpha, I}|\alpha, I\rangle$ keeping only terms to first order in ϵ :

$$\begin{aligned} & \sum_i c_{I,i}^{(0)} \hat{H}^{(0)}|\alpha, i\rangle + \epsilon \sum_i c_{I,i}^{(0)} \hat{H}^{(1)}|\alpha, i\rangle + \epsilon \sum_{i, \beta \neq \alpha} c_{I,\beta,i}^{(1)} \hat{H}^{(0)}|\beta, i\rangle \\ &= \sum_i c_{I,i}^{(0)} E_{\alpha}^{(0)}|\alpha, i\rangle + \epsilon \sum_i c_{I,i}^{(0)} E_{\alpha, I}^{(1)}|\alpha, i\rangle + \epsilon \sum_{i, \beta \neq \alpha} c_{I,\beta,i}^{(1)} E_{\alpha}^{(0)}|\beta, i\rangle \end{aligned}$$

Using (1), we can replace $\hat{H}^{(0)}$ with its eigenvalue wherever it appears. The first term on each side is then the same, so these cancel, and we get

$$\sum_i c_{I,i}^{(0)} E_{\alpha, I}^{(1)}|\alpha, i\rangle = \sum_i c_{I,i}^{(0)} \hat{H}^{(1)}|\alpha, i\rangle + \sum_{i, \beta \neq \alpha} c_{I,\beta,i}^{(1)} (E_{\beta}^{(0)} - E_{\alpha}^{(0)})|\beta, i\rangle \quad (2)$$

Now recall that different energy eigenstates are necessarily orthogonal, so in particular

$$\langle \alpha, J | \alpha, I \rangle = \delta_{J, I}$$

This will hold at every order in ϵ , so if we act on (2) with ${}^{(0)}\langle \alpha, J |$, the LHS gives zero, as does the second term on the RHS, since the sum excludes $\beta = \alpha$. We therefore obtain

$${}^{(0)}\langle \alpha, J | \hat{H}^{(1)} | \alpha, I \rangle^{(0)} = E_{\alpha, I}^{(1)} \delta_{J, I}$$

In other words, $\hat{H}^{(1)}$ is diagonal in the basis $|\alpha, I\rangle^{(0)}$, and the first order corrections to the energies are

$$E_{\alpha, I}^{(1)} = {}^{(0)}\langle \alpha, I | \hat{H}^{(1)} | \alpha, I \rangle^{(0)} \quad (3)$$

So, in summary:

- In each eigenspace of $\hat{H}^{(0)}$, choose quantum numbers I corresponding to operators which commute with $\hat{H}^{(1)}$.
- The first order energy corrections are then given by (3).
- Note that, although we can also use (2) to calculate the first order corrections to the eigenstates, we don't need them to find the first order shifts in the eigenvalues.

Atomic physics

As with most real-life systems, there are many different interactions acting simultaneously in an atom. However they are not all equally important; if we can understand the strongest interactions first, then perturbation theory will let us deal with the rest approximately.

The crudest approximation we can make for an atom is that the electrons move in a central field, sourced by the nucleus and the electrons themselves. The Hamiltonian in this approximation is

$$\hat{H}^{(0)} = \frac{e}{4\pi\epsilon_0} \sum_i \left(-\frac{Z}{|\hat{\mathbf{r}}_i|} + \tilde{Q}(|\hat{\mathbf{r}}_i|) \right)$$

where \tilde{Q} represents the central part of the electron-electron repulsion. Since this is a spherically symmetric potential which falls to zero at infinity, the analysis is very similar to that for hydrogen: each electron is labelled by the quantum numbers n, l, m_l, m_s . The main difference is that the energy now depends on both n and l , due to screening effects, represented by the \tilde{Q} term.

Residual Coulomb interaction

In the B1 course at Oxford, we consider only relatively small atoms, for which the next strongest interaction is the residual (non-central) Coulomb repulsion between electrons. The corresponding term in the Hamiltonian is

$$\epsilon_1 \hat{H}^{(1)} = \frac{e}{4\pi\epsilon_0} \sum_i \left(\sum_{j>i} \frac{e}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|} - \tilde{Q}(|\hat{\mathbf{r}}_i|) \right)$$

The angular momentum operator $\hat{\mathbf{l}}_i$ associated with a particular electron does *not* commute with this operator (exercise), so the separate values l and m_l for each electron are not good quantum numbers. However, we can define the total orbital angular momentum operator:

$$\hat{\mathbf{L}} = \sum_i \hat{\mathbf{l}}_i$$

$\hat{\mathbf{L}}$ commutes with both $\hat{H}^{(0)}$ and $\hat{H}^{(1)}$ (essentially because the total system is rotationally invariant), so L and M_L are good quantum numbers i.e. we can use them to label the energy eigenstates. You should convince yourself that this gives the same number of states as specifying l and m_l for each electron separately; we have simply chosen a better basis for the same Hilbert space. Similarly, we can replace the separate values of m_s with S and M_S for the whole system. At this stage either choice is fine, because we have not taken spin interactions into account.

Spin-orbit interaction

The next interaction to consider is the spin-orbit interaction, the Hamiltonian for which is

$$\epsilon_2 \hat{H}_2 \propto \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$$

The individual components of $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ do not commute with \hat{H}_2 , but $|\hat{\mathbf{L}}|^2$ and $|\hat{\mathbf{S}}|^2$ do. Therefore L and S are still good quantum numbers, but M_L and M_S are not. But if we define the total angular momentum $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$, then it is easy to check that $\hat{\mathbf{J}}$ commutes with \hat{H}_2 , since

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{1}{2}(|\hat{\mathbf{J}}|^2 - |\hat{\mathbf{L}}|^2 - |\hat{\mathbf{S}}|^2)$$

The values of S, L, J, M_J then uniquely specify a state, so we have our complete set of quantum numbers. (Once again, you can check that we are describing the same number of states at each step.)

Of course this is not the end of the story for atomic structure, but hopefully it is enough to illustrate the concepts.