Degenerate perturbations

$H^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$, with degeneracy
$E_1^{(0)} = E_2^{(0)} = \cdots = E_d^{(0)}$.
As in the nondegenerate case, $E_n \stackrel{\lambda\to 0}{\to} E_n^{(0)}$, but ψ_n can go to any linear combination of the degenerate functions:

$$\psi_n \stackrel{\lambda\to 0}{\to} \sum_i^d c_i\psi_i^{(0)} \equiv \phi_n^{(0)}.$$

The expansions for $i = 1, 2, \cdots, d$ are

$$\psi_n = \phi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots$$

$$E_n = E_1^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots$$

The zero-order equation

$$H^{(0)}\phi_n^{(0)} = E_1^{(0)}\phi_n^{(0)} \quad n = 1, \cdots, d$$

The 1st-order equation

$$H^{(0)}\psi_n^{(1)} + H'\phi_n^{(0)} = E_1^{(0)}\psi_n^{(1)} + E_n^{(1)}\phi_n^{(0)} \quad n = 1, \cdots, d$$

Scalar product with $\langle\psi_j^{(0)}|, \;\; 1 \le j \le d$ gives

$$\langle\psi_j^{(0)}|H^{(0)}|\psi_n^{(1)}\rangle + \langle\psi_j^{(0)}|H'|\phi_n^{(0)}\rangle =$$

$$= E_1^{(0)}\langle\psi_j^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}\langle\psi_j^{(0)}|\phi_n^{(0)}\rangle.$$

The first terms on both sides are equal and cancel out, leaving

$$\langle\psi_j^{(0)}|H'|\phi_n^{(0)}\rangle = E_n^{(1)}\langle\psi_j^{(0)}|\phi_n^{(0)}\rangle.$$

Replacing $|\phi_n^{(0)}\rangle$ by $\sum_{i=1}^{d} c_i|\psi_i^{(0)}\rangle$ gives

$$\sum_{i=1}^{d} c_i \left(\langle\psi_j^{(0)}|H'|\psi_i^{(0)}\rangle - E_n^{(1)}\delta_{ij} \right) = 0,$$

d secular equations in d unknown. Solved in the usual manner, they yield d first-order energy corrections $E_n^{(1)}$ and d vectors of coefficients which give the corresponding $\phi_n^{(0)}$.

Meaning of $\phi_n^{(0)}$: Without the perturbation, any linear combination of the degenerate zero-order functions $\psi_i^{(0)}$ is an eigenfunction of $H^{(0)}$, and all of the combinations are equally acceptable. The perturbation breaks this degeneracy. When the perturbation is decreased and is very close (but not equal) to zero, the perturbed wavefunction is very close to a specific linear combination of $\psi_i^{(0)}$. This linear combination is $\phi_n^{(0)}$.

By solving the secular equations above we diagonalized the H' matrix in the space of the degenerate zero-order functions $\psi_n^{(0)}$. The functions which diagonalize H' are $\phi_n^{(0)}$. This gives

$$\langle\phi_i^{(0)}|H'|\phi_j^{(0)}\rangle = E_i^{(1)}\delta_{ij}, \quad i, j = 1, \cdots, d.$$

All integrals of H' between $\phi_i^{(0)}$ and $\phi_j^{(0)}$ vanish if $i \neq j$. Using the $\phi_i^{(0)}$ set, the usual formulas of perturbation theory are therefore applicable.

To sum up, we treat degenerate zero-order functions (for which integrals of $H^{(1)}$ do not vanish) by first diagonalizing the matrix of H' in the degenerate subspace. We then use the linear combinations which diagonalize the perturbation; the integrals of the perturbation between these linear combinations vanish, so we can apply the usual nondegenerate method.

Stark effect in the hydrogen atom

The energy levels of atoms and molecules shift when an electric field is applied. This is called the Stark effect. We will discuss the Stark effect on the two lowest levels $n = 1, 2$ of the hydrogen atoms.

The Hamiltonian of the H atom in an electric field $\mathcal{E}$ is

$$H = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{r} + ez\mathcal{E},$$

where μ is the reduced electron mass and the z coordinate is in the direction of $\mathcal{E}$.

The energies of the zero-order $H^{(0)} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{r}$ are $E_n^{(0)} = -\frac{\mu e^4}{2\hbar^2 n^2}, \quad n = 1, 2, \cdots$.

Ground state ($n = 1$):

The first order correction is $\langle\psi_{1s}|ez\mathcal{E}|\psi_{1s}\rangle$. It vanishes because of symmetry: ψ_{1s} is symmetric to inversion ($x, y, z \rightarrow -x, -y, -z$) and z is antisymmetric, so the integrand is antisymmetric and the integral is 0.

Second order: $\lambda^2 E_{1s}^{(2)} = \sum_{nlm\neq 100} \frac{|\langle\psi_{nlm}|e\mathcal{E}z|\psi_{1s}\rangle|^2}{E_1^{(0)} - E_n^{(0)}}$. This is the quadratic Stark effect, proportional to $\mathcal{E}^2$.

This system is simple enough for the first-order equation to be soluble exactly, giving $E_1^{(2)} = -\frac{9}{4}a_0^3 e^2 \mathcal{E}^2$.

The physical picture is as follows: the electric field polarizes the atomic charge, creating an induced dipole moment $d = \alpha\mathcal{E}$, which in turn interacts with the field. The energy shift is $-\frac{1}{2}\alpha\mathcal{E}^2$. α is the polarizability, given for the ground state of hydrogen by $\alpha = \frac{9}{2}a_0^3$.

Excited state $(n = 2)$

This state is degenerate, with four functions (ignoring spin) having the same energy. The four functions in the usual nlm representation are

$$
\begin{aligned}
\psi_1^{(0)} &\equiv \psi_{200} \quad (2s) \\
\psi_2^{(0)} &\equiv \psi_{210} \quad (2p_0) \\
\psi_3^{(0)} &\equiv \psi_{211} \quad (2p_1) \\
\psi_4^{(0)} &\equiv \psi_{21-1} \quad (2p_{-1})
\end{aligned}
$$

Applying degenerate perturbation theory, we define the zero-order functions $\phi_j^{(0)} = \sum_1^4 c_{ji}\psi_i^{(0)}$.

The secular determinant is of order 4,

$$\det\left|H_{ji}^{(1)} - E^{(1)}\delta_{ji}\right| = 0, \quad H_{ji}^{(1)} = \langle\psi_j^{(0)}|ez\mathcal{E}|\psi_i^{(0)}\rangle.$$

Since $z = r\cos\theta$ does not depend on the φ angle, $H_{ji}^{(1)}$ vanishes for $m \neq m'$. It also vanishes (parity!) for $j = i$. The only non-vanishing integral is between the $2s$ and $2p_0$ orbitals, which is $\langle\psi_{2s}|ez\mathcal{E}|\psi_{2p_0}\rangle = 3a_0e\mathcal{E}$. The secular determinant is

$$\begin{vmatrix} -E^{(1)} & 3a_0e\mathcal{E} & 0 & 0 \\ 3a_0e\mathcal{E} & -E^{(1)} & 0 & 0 \\ 0 & 0 & -E^{(1)} & 0 \\ 0 & 0 & 0 & -E^{(1)} \end{vmatrix} = 0$$

The determinant shows that $2p_1$ and $2p_{-1}$ do not mix (in zero order) with any states. This could have been deduced without writing the determinant, since their m value is different from all other functions. They will therefore show a quadratic Stark effect. Solving the secular determinant gives for the first two functions $E^{(1)} = E^{(0)} \pm 3a_0 e\mathcal{E}$, which is proportional to the first power of the field. This is the linear Stark effect, which (if non-zero) is larger than the quadratic.

The $n = 2$ levels of H are split by $\mathcal{E}$ to three groups: the $2p_{\pm 1}$ levels stay degenerate, shift quadratically. The other two levels show a larger linear shift, one going up and the other down. Going back to the secular equations, the zero-order functions corresponding to these levels are

$$\phi_1 = (\psi_{2s} - \psi_{2p_0})/\sqrt{2}$$

$$\phi_2 = (\psi_{2s} + \psi_{2p_0})/\sqrt{2}.$$