Corrections to the hydrogen spectrum

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1 Perturbation theory

Perturbations in quantum mechanics fall into two categories: stationary state, and time-dependent. Within these special techniques must be applied when the energy levels are degenerate.

1.1 Non-degenerate, stationary state perturbation theory

Suppose we have a Hamiltonian, $\hat{H} = \hat{H}_0 + \lambda\hat{V}$ where we may regard the effect of $\hat{V}$ as small compared to the unperturbed Hamiltonian $\hat{H}_0$.

The simplest case arises if $\hat{V}$ commutes with the original Hamiltonian, $\left[\hat{H}_0, \hat{V}\right] = 0$. Then the original basis may be chosen to give simultaneous eigenvalues so that

$$\hat{V}\left|E_n^{(0)}\right\rangle = V\left|E_n^{(0)}\right\rangle$$

the stationary state Schrödinger equation gives

$$\hat{H}\left|E_n^{(0)}\right\rangle = \left(E_n^{(0)} + V\right)\left|E_n^{(0)}\right\rangle$$

and we are done.

More typically, the perturbation $\hat{V}$ will have nonvanishing matrix elements between different original states, $\left\langle E_m^{(0)}\right|\hat{V}\left|E_n^{(0)}\right\rangle \neq 0$. Then we proceed as follows. Expand both the energies and the energy eigenstates in a series,

$$\begin{aligned} E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots \\ |E_n\rangle &= \left(\left|E_n^{(0)}\right\rangle + \lambda\left|E_n^{(1)}\right\rangle + \lambda^2\left|E_n^{(2)}\right\rangle + \cdots\right) \end{aligned}$$

where $\hat{H}_0\left|E_n^{(0)}\right\rangle = E_n^{(0)}\left|E_n^{(0)}\right\rangle$, and substitute into the stationary state Schrödinger equation, $\hat{H}\,|E\rangle = E\,|E\rangle$.

The left side of the equation expands as

$$\begin{aligned} \hat{H}\,|E\rangle &= \hat{H}_0\left(\left|E_n^{(0)}\right\rangle + \lambda\left|E_n^{(1)}\right\rangle + \lambda^2\left|E_n^{(2)}\right\rangle + \cdots\right) \\ &\quad +\lambda\hat{V}\left(\left|E_n^{(0)}\right\rangle + \lambda\left|E_n^{(1)}\right\rangle + \lambda^2\left|E_n^{(2)}\right\rangle + \cdots\right) \\ &= \hat{H}_0\left|E_n^{(0)}\right\rangle + \lambda\hat{H}_0\left|E_n^{(1)}\right\rangle + \lambda\hat{V}\left|E_n^{(0)}\right\rangle \\ &\quad +\lambda^2\hat{H}_0\left|E_n^{(2)}\right\rangle + \lambda^2\hat{V}\left|E_n^{(1)}\right\rangle + \cdots \end{aligned}$$

while the right expands as

$$E\,|E\rangle = E_n^{(0)}\left(\left|E_n^{(0)}\right\rangle + \lambda\left|E_n^{(1)}\right\rangle + \lambda^2\left|E_n^{(2)}\right\rangle + \cdots\right)$$

$$
\begin{aligned}
&+\lambda E_n^{(1)}\left(\left|E_n^{(0)}\right\rangle+\lambda\left|E_n^{(1)}\right\rangle+\lambda^2\left|E_n^{(2)}\right\rangle+\cdots\right)\\
&+\lambda^2 E_n^{(2)}\left(\left|E_n^{(0)}\right\rangle+\lambda\left|E_n^{(1)}\right\rangle+\lambda^2\left|E_n^{(2)}\right\rangle+\cdots\right)+\cdots\\
=\;& E_n^{(0)}\left|E_n^{(0)}\right\rangle\\
&+\lambda E_n^{(0)}\left|E_n^{(1)}\right\rangle+\lambda E_n^{(1)}\left|E_n^{(0)}\right\rangle\\
&+\lambda^2 E_n^{(0)}\left|E_n^{(2)}\right\rangle+\lambda^2 E_n^{(1)}\left|E_n^{(1)}\right\rangle+\lambda^2 E_n^{(2)}\left|E_n^{(0)}\right\rangle\\
&+\cdots
\end{aligned}
$$

Equating order by order,

$$
\begin{aligned}
\hat{H}_0\left|E_n^{(0)}\right\rangle &= E_n^{(0)}\left|E_n^{(0)}\right\rangle\\
\lambda\left(\hat{H}_0\left|E_n^{(1)}\right\rangle+\hat{V}\left|E_n^{(0)}\right\rangle\right) &= \lambda\left(E_n^{(0)}\left|E_n^{(1)}\right\rangle+E_n^{(1)}\left|E_n^{(0)}\right\rangle\right)\\
\lambda^2\left(\hat{H}_0\left|E_n^{(2)}\right\rangle+\hat{V}\left|E_n^{(1)}\right\rangle\right) &= \lambda^2\left(E_n^{(0)}\left|E_n^{(2)}\right\rangle+E_n^{(1)}\left|E_n^{(1)}\right\rangle+E_n^{(2)}\left|E_n^{(0)}\right\rangle\right)
\end{aligned}
$$

The first equation is identically satisfied. For the second, bring an unperturbed bra, $\left\langle E_n^{(0)}\right|$, in from the left

$$
\left\langle E_n^{(0)}\right|\hat{H}_0\left|E_n^{(1)}\right\rangle+\left\langle E_n^{(0)}\right|\hat{V}\left|E_n^{(0)}\right\rangle=\left\langle E_n^{(0)}\right|E_n^{(0)}\left|E_n^{(1)}\right\rangle+\left\langle E_n^{(0)}\right|E_n^{(1)}\left|E_n^{(0)}\right\rangle
$$

We assume the different perturbed kets are orthogonal to one another and to the original kets of the same energy, so the first term on each side vanishes leaving

$$
E_n^{(1)}=\left\langle E_n^{(0)}\right|\hat{V}\left|E_n^{(0)}\right\rangle
$$

as the first order correction to the energy.

To find the first order correction to the state, we must invert $\left(\hat{H}_0-E_n^{(0)}\right)$:

$$
\begin{aligned}
\hat{H}_0\left|E_n^{(1)}\right\rangle+\hat{V}\left|E_n^{(0)}\right\rangle &= E_n^{(0)}\left|E_n^{(1)}\right\rangle+E_n^{(1)}\left|E_n^{(0)}\right\rangle\\
\left(\hat{H}_0-E_n^{(0)}\right)\left|E_n^{(1)}\right\rangle &= E_n^{(1)}\left|E_n^{(0)}\right\rangle-\hat{V}\left|E_n^{(0)}\right\rangle
\end{aligned}
$$

Before we invert, we project orthogonal to the $\left|E_n^{(0)}\right\rangle$ state. This loses nothing since the state we seek must be orthogonal to $\left|E_n^{(0)}\right\rangle$ anyway – notice on the right that any part of $\left|E_n^{(1)}\right\rangle$ proportional to $\left|E_n^{(0)}\right\rangle$ will be anihilated: $\left(\hat{H}_0-E_n^{(0)}\right)\left|E_n^{(0)}\right\rangle=0$. Let $\hat{P}_{n\perp}^{(0)}$ be the orthogonal operator, so that $\hat{P}_{n\perp}^{(0)}\left|E_n^{(0)}\right\rangle=0$. Then, noticing that

$$
\hat{P}_{n\perp}^{(0)}\left(\hat{H}_0-E_n^{(0)}\right)=\hat{H}_0-E_n^{(0)}
$$

since $\hat{H}_0-E_n^{(0)}$ already anihilates $\left|E_n^{(0)}\right\rangle$, we have

$$
\begin{aligned}
\left(\hat{H}_0-E_n^{(0)}\right)\left|E_n^{(1)}\right\rangle &= \left(-\hat{P}_{n\perp}^{(0)}\hat{V}\left|E_n^{(0)}\right\rangle\right)\\
\left|E_n^{(1)}\right\rangle &= \frac{1}{E_n^{(0)}-\hat{H}_0}\hat{P}_{n\perp}^{(0)}\hat{V}\left|E_n^{(0)}\right\rangle
\end{aligned}
$$

We may write the projection operator as

$$
\hat{P}_{n\perp}^{(0)}=\sum_{m=0,m\neq n}^{\infty}\left|E_m^{(0)}\right\rangle\left\langle E_m^{(0)}\right|
$$

so that

$$\begin{aligned}
\left|E_n^{(1)}\right\rangle &= \sum_{m=0,m\neq n}^{\infty} \frac{1}{E_n^{(0)} - \hat{H}_0} \left|E_m^{(0)}\right\rangle \left\langle E_m^{(0)}\right| \hat{V} \left|E_n^{(0)}\right\rangle \\
&= \sum_{m=0,m\neq n}^{\infty} \frac{1}{E_n^{(0)} - E_m^{(0)}} \left|E_m^{(0)}\right\rangle \left\langle E_m^{(0)}\right| \hat{V} \left|E_n^{(0)}\right\rangle \\
&= \sum_{m=0,m\neq n}^{\infty} \frac{\left\langle E_m^{(0)}\right| \hat{V} \left|E_n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}} \left|E_m^{(0)}\right\rangle
\end{aligned}$$

This gives the expansion of the first order perturbation in terms of the original basis kets, and the matrix elements of the perturbation.

To find the second order corrections, we move to

$$\hat{H}_0 \left|E_n^{(2)}\right\rangle + \hat{V} \left|E_n^{(1)}\right\rangle = E_n^{(0)} \left|E_n^{(2)}\right\rangle + E_n^{(1)} \left|E_n^{(1)}\right\rangle + E_n^{(2)} \left|E_n^{(0)}\right\rangle$$

Brining in an unperturbed bra as before gives

$$E_m^{(2)} = E_n^{(2)} \delta_{mn} = \left\langle E_m^{(0)}\right| \hat{V} \left|E_n^{(1)}\right\rangle$$

and we need the first perturbation to proceed. Substituting,

$$\begin{aligned}
E_m^{(2)} &= \left\langle E_m^{(0)}\right| \hat{V} \sum_{k=0,k\neq n}^{\infty} \frac{\left\langle E_k^{(0)}\right| \hat{V} \left|E_n^{(0)}\right\rangle}{E_n^{(0)} - E_k^{(0)}} \left|E_k^{(0)}\right\rangle \\
&= \sum_{k=0,k\neq n}^{\infty} \frac{\left\langle E_m^{(0)}\right| \hat{V} \left|E_k^{(0)}\right\rangle \left\langle E_k^{(0)}\right| \hat{V} \left|E_n^{(0)}\right\rangle}{E_n^{(0)} - E_k^{(0)}}
\end{aligned}$$

To find the state, we repeat the procedure,

$$\begin{aligned}
\hat{P}_{n\perp}^{(0)} \left(\hat{H}_0 - E_n^{(0)}\right) \left|E_n^{(2)}\right\rangle &= \hat{P}_{n\perp}^{(0)} \left(E_n^{(1)} - \hat{V}\right) \left|E_n^{(1)}\right\rangle + E_n^{(2)} \hat{P}_{n\perp}^{(0)} \left|E_n^{(0)}\right\rangle \\
\left(\hat{H}_0 - E_n^{(0)}\right) \left|E_n^{(2)}\right\rangle &= \hat{P}_{n\perp}^{(0)} \left(E_n^{(1)} - \hat{V}\right) \left|E_n^{(1)}\right\rangle
\end{aligned}$$

Inverting and substituting the first order correction,

$$\begin{aligned}
\left|E_n^{(2)}\right\rangle &= \frac{1}{\hat{H}_0 - E_n^{(0)}} \hat{P}_{n\perp}^{(0)} \left(E_n^{(1)} - \hat{V}\right) \sum_{m=0,m\neq n}^{\infty} \frac{\left\langle E_m^{(0)}\right| \hat{V} \left|E_n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}} \left|E_m^{(0)}\right\rangle \\
&= \frac{1}{\hat{H}_0 - E_n^{(0)}} \sum_{k\neq n} \left|E_k^{(0)}\right\rangle \left\langle E_k^{(0)}\right| \left(E_n^{(1)} - \hat{V}\right) \sum_{m\neq n} \frac{\left\langle E_m^{(0)}\right| \hat{V} \left|E_n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}} \left|E_m^{(0)}\right\rangle \\
&= \sum_{k\neq n} \sum_{m\neq n} \frac{\left\langle E_k^{(0)}\right| \hat{V} \left|E_m^{(0)}\right\rangle}{E_n^{(0)} - E_k^{(0)}} \frac{\left\langle E_m^{(0)}\right| \hat{V} \left|E_n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}} \left|E_k^{(0)}\right\rangle
\end{aligned}$$

Notice that we have a product of matrix elements, $\sum_{m\neq n} \left\langle E_k^{(0)}\right| \hat{V} \left|E_m^{(0)}\right\rangle \left\langle E_m^{(0)}\right| \hat{V} \left|E_n^{(0)}\right\rangle$, effectively multiplying two copies$V_{km} V_{mn}$. Higher orders give corresponding products, weighted by the energy differences.

2 Fine structure

Corrections to the hydrogen spectrum on the order of $\alpha^2 \approx \left(\frac{1}{137}\right)^2$ are called *fine structure*, where the constant $\alpha \equiv \frac{e^2}{\hbar c}$ is called the *fine structure constant*. These include:

1. Spin-Orbit coupling
2. Relativistic kinetic correction

There are also two corrections at this order to the $l = 0$ state energy:

1. Darwinian
2. Lamb shift

We explore the first two in detail.

2.1 Spin-Orbit coupling

In the rest frame of the electron, the proton orbits, producing a magnetic field at the position of the electron. Boosting the electric field from the rest frame of the proton to the instantaneous frame of the electron,

$$\begin{aligned} \mathbf{B}_{\perp}^{'} &= \gamma \left(\mathbf{B}_{\perp} + \boldsymbol{\beta} \times \mathbf{E} \right) \\ &= \gamma \boldsymbol{\beta} \times \mathbf{E} \\ &\approx \frac{1}{c} \mathbf{v} \times \mathbf{E} \end{aligned}$$

where, since this correction is already small, we neglect the correction due to γ. The electric field is given by the gradient of the potential,

$$\begin{aligned} \mathbf{E} &= -\frac{1}{e} \boldsymbol{\nabla} V(r) \\ &= -\frac{\mathbf{r}}{er} \frac{dV}{dr} \end{aligned}$$

Therefore,

$$\begin{aligned} \mathbf{B}_{\perp}^{'} &= \frac{1}{c} \mathbf{v} \times \frac{\mathbf{r}}{er} \frac{dV}{dr} \\ &= -\frac{1}{mc} \frac{1}{er} \frac{dV}{dr} \mathbf{L} \end{aligned}$$

The electron has a magnetic moment, $\boldsymbol{\mu} = \frac{e}{mc} \mathbf{S}$, which we take to be oriented relative to this field, so we expect an interaction with the magnetic field of

$$\begin{aligned} H_{LS} &= -\boldsymbol{\mu} \cdot \mathbf{B} \\ &= \frac{1}{m^2 c^2} \frac{1}{r} \frac{dV}{dr} \mathbf{L} \cdot \mathbf{S} \end{aligned}$$

A fuller treatment including the Thomas precession is presented in Jackson. It shows that because the frame of the electron is accelerating this result requires an additional factor of $\frac{1}{2}$, so the actual spin-orbit Hamiltonian operator is

$$\hat{H}_{LS} = \frac{1}{2m^2 c^2} \frac{1}{r} \frac{dV}{dr} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$$

Now consider our hydrogen states,

$$\left| E, l, m_l, s = \frac{1}{2}, m_s \right\rangle = |E, l\rangle \otimes |l, m_l\rangle \otimes \left| \frac{1}{2}, m_s \right\rangle$$

We can make these same states into eigenstates of $\hat{H}_{LS}$ as well by adding the angular momenta:

$$|l, m_l\rangle \otimes \left|\frac{1}{2}, m_s\right\rangle \Rightarrow |j, m\rangle$$

with j taking values $l + \frac{1}{2}$ and $l - \frac{1}{2}$ (there are $2 \times (2l+1)$ states on the left and with $j = l + \frac{1}{2}$ there are $2\left(l + \frac{1}{2}\right) + 1 = 2l + 2$; we also require $j = l - \frac{1}{2}$ to give the remaining $2\left(l - \frac{1}{2}\right) + 1 = 2l$ states). Since $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$, we may write the $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ operator as

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

This does not change the states, because each of $\hat{\mathbf{J}}^2, \hat{\mathbf{L}}^2, \hat{\mathbf{S}}^2$ commutes with $\hat{J}_z$. We may therefore label our states by

$$|E, j, l, s, , j_z\rangle$$

instead of $|E, l, m_l, s, m_s\rangle$ and they remain eigenstates of both $\hat{H}_0$ and $\hat{H}_{LS}$

The correction to the energy is now immediate,

$$\begin{aligned}
\Delta E &= \langle E, j, l, s, , j_z| \hat{H}_{LS} |E, j, l, s, , j_z\rangle \\
&= \langle E, j, l, s, , j_z| \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\frac{1}{2}\left(\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2\right) |E, j, l, s, , j_z\rangle \\
&= \frac{1}{2m^2c^2}\frac{\hbar^2}{2}\left(j(j+1) - l(l+1) - \frac{3}{4}\right) \langle E, j, l, s, , j_z| \frac{1}{r}\frac{dV}{dr} |E, j, l, s, , j_z\rangle
\end{aligned}$$

The angular momentum factor takes values

$$\begin{aligned}
\frac{1}{2m^2c^2}\frac{\hbar^2}{2}(l) \quad for \quad j = l + \frac{1}{2} \\
-\frac{1}{2m^2c^2}\frac{\hbar^2}{2}(l+1) \quad for \quad j = l - \frac{1}{2}
\end{aligned}$$

while the remaining expectation is computed using the radial wave functions,

$$\langle E, j, l, s, , j_z| \frac{1}{r}\frac{dV}{dr} |E, j, l, s, , j_z\rangle = \langle R_{n,l}| \frac{1}{r}\frac{dV}{dr} |R_{n,l}\rangle$$

Since the gradient, $-\frac{dV}{dr}$ is on the order of $\frac{e}{r^2}$ and r is on the order of the Bohr radius, a_0, the magnitude of the spin-orbit coupling correction is approximately

$$\begin{aligned}
\Delta E &\sim \frac{1}{2m^2c^2}\frac{\hbar^2}{2}\frac{e}{a_0^3} \\
&\sim \frac{1}{2\left(.5Mev\right)^2}\frac{\hbar^2c^2}{2}\frac{e}{a_0^3} \\
&\sim \frac{1}{.5\left(Mev\right)^2}\frac{\left(200Mev \cdot fm\right)^2}{2}\frac{1eV}{\left(5 \times 10^{-11}m\right)^2} \\
&\sim \frac{4 \times 10^4 \times 10^{-30}m^2}{\left(5 \times 10^{-11}m\right)^2}eV \\
&\sim \frac{4 \times 10^{-26}}{25 \times 10^{-22}}eV \\
&\sim 1.6 \times 10^{-5}\, eV
\end{aligned}$$

2.2 Relativistic kinetic correction

The kinetic energy of the electron is given by

$$\begin{aligned} KE &= \sqrt{p^2c^2 + m^2c^4} - mc^2 \\ &= mc^2\left(\sqrt{1 + \frac{p^2}{m^2c^2}} - 1\right) \end{aligned}$$

Expanding the square root, $(1+x)^{\frac{1}{2}} = 1 + \frac{1}{2}x + \frac{1}{2}\left(\frac{1}{2}\left(-\frac{1}{2}\right)\right)x^2$

$$\begin{aligned} KE &= mc^2\left(1 + \frac{1}{2}\frac{p^2}{m^2c^2} - \frac{1}{8}\left(\frac{p^2}{m^2c^2}\right)^2 + \cdots - 1\right) \\ KE &= \frac{p^2}{2m} - \frac{1}{8}\frac{\left(p^2\right)^2}{m^3c^2} + \cdots \end{aligned}$$

The ratio of the second term to the first is

$$\frac{1}{4}\frac{p^2}{m^2c^2} \sim \frac{p^2}{2m}\frac{1}{2mc^2} \sim 10eV \cdot \frac{1}{1MeV} \sim 10^{-5}$$

To evaluate this contribution, write it as

$$\begin{aligned} -\frac{1}{8}mc^2\left(\frac{p^2}{m^2c^2}\right)^2 &= -\frac{1}{2mc^2}m\left(\frac{p^2}{2m}\right) \\ &= -\frac{1}{2mc^2}\left(H - V\right)^2 \end{aligned}$$

The energy correction is therefore

$$\begin{aligned} \Delta E &= -\frac{1}{2mc^2}\left\langle E, j, l, s, , j_z\right|\left(\hat{H} - \frac{e^2}{r}\right)^2\left|E, j, l, s, , j_z\right\rangle \\ &= -\frac{1}{2mc^2}\left(E^2 - 2Ee^2\left\langle R_{n,l}\right|\frac{1}{r}\left|R_{n,l}\right\rangle + e^4\left\langle R_{n,l}\right|\frac{1}{r^2}\left|R_{n,l}\right\rangle\right) \end{aligned}$$

3 Hyperfine structure

Hyperfine structure takes into account the coupling of the magnetic moment of the proton to the magnetic field produced by the motion of the electron. This is reduced by a factor of $\frac{m_e}{m_p} \sim \frac{1}{1836}$ from the fine structure effect. Hyperfine structure also includes the interaction of the two dipole fields created by the magnetic moments of the electron and proton, and in more complex atoms, the quadrupole moments of the charges.