Time-independent perturbation theory

Let's assume we are dealing with a Hamiltonian of the form

$$H = H^0 + H'$$

where we know the solutions to:

$$H^0\psi_n = E_n^0\psi_n$$

Generally we would write the corrected energies and states as*:

$$E_n = E_n^0 + E_n^1 + E_n^2 + \cdots$$
$$\psi_n = \psi_n^0 + \psi_n^1 + \psi_n^2 + \cdots$$

Non-degenerate:

If $E_n^0 = E_m^0 \implies m = n$ then we can use non-degenerate perturbation theory. In this case the energy corrections take the following form:

$$E_n^1 = \langle\psi_n^0|\, H' \,|\psi_n^0\rangle$$
$$E_n^2 = \sum_{m\neq n} \frac{|\langle\psi_m^0|\, H' \,|\psi_n^0\rangle|^2}{E_n^0 - E_m^0}$$

And the first order state correction is given by:

$$\psi_n^1 = \sum_{m\neq n} \frac{\langle\psi_m^0|\, H' \,|\psi_n^0\rangle}{E_n^0 - E_m^0}\psi_m^0$$

Degenerate:

Suppose we are dealing with n-fold degeneracy, which means that there are n states, ψ_i^0, such that

$$H^0\psi_i^0 = E^0\psi_i^0, \quad \langle\psi_i^0|\psi_j^0\rangle = \delta_{ij}$$

Now we define the perturbation matrix, W, as:

$$W_{ij} = \langle\psi_i^0|\, H' \,|\psi_j^0\rangle$$

Note that $W_{ij} = W_{ji}^*$ because H' is hermitian. Now, the first order corrections to the energies will be given by the eigenvalues of W.

Good states:

The perturbation matrix will usually not be a diagonal matrix in the $\{\psi_i\}$ basis. However, we can use linear combinations of ψ_i to find the "good"states, i.e. states for which W is diagonal, if these states are used as the basis. Thus we need to do the following:

1. Calculate W
2. Determine W's eigenvalues and eigenvectors
3. The eigenvectors are the "good"states†

Given $\{\psi_i\}$ it does not make sense to ask "whose eigenvalues follow which path in the perturbation diagram". However, once we have determined the "good"states, this question makes more sense to ask.

The fine structure of the hydrogen atom (and more) are shown in the Appendix.

Time-dependent perturbation theory

Let us assume we are describing a two-level system, where the two states are ψ_a and ψ_b, and that $E_a < E_b$. We begin in the state:

$$\Psi(0) = c_a\psi_a + c_b\psi_b, \quad |c_a|^2 + |c_b|^2 = 1$$

Then we know how the system evolves in time (just multiply by the wiggle factors). Now we perturb the system, with a time dependent perturbation:

$$H(t) = H_0 + H'(t)$$

Then it would make sense to make the coefficients time dependent:

$$\Psi(t) = c_a(t)\psi_a e^{-iE_at/\hbar} + c_b(t)\psi_b e^{-iE_bt/\hbar}$$

By plugging this into the Schrödinger equation and using some smart tricks, one gets

$$\dot{c}_a = -\frac{i}{\hbar}\left(c_aH'_{aa} + c_bH'_{ab}e^{-i\omega_0t}\right)$$
$$\dot{c}_b = -\frac{i}{\hbar}\left(c_aH'_{ba}e^{i\omega_0t} + c_bH'_{bb}\right)$$

where

$$\omega_0 \equiv \frac{E_b - E_a}{\hbar}$$
$$H'_{ij} \equiv \langle\psi_i|\, H' \,|\psi_j\rangle$$

However, very often $H'_{ii} = 0$, which simplifies the calculations significantly. At this point the book assumes this is true, therefore I will do the same. Additionally, the perturbation must be much smaller than

---

* note that the superscript denotes the order of the correction, and should therefore *not* be interpreted as an exponent.

† The eigenvectors tell you which linear combination of the original states gives the "good"state.

the unperturbed Hamiltonian. Assume we begin in the state described by

$$c_a(t_0) = 1, \quad c_b(t_0) = 0$$

without a perturbation the system will stay in this state indefinitely, therefore to **zeroth order**, we get:

$$c_a^{(0)}(t) = 1, \quad c_b^{(0)}(t) = 0$$

First order:

$$c_a^{(1)}(t) = 1$$
$$c_b^{(1)}(t) = -\frac{i}{\hbar}\int_0^t H'_{ba}(t')e^{i\omega_0 t'}\,\mathrm{d}t'$$

Second order:

$$c_a^{(2)}(t) = 1 - \frac{1}{\hbar^2}\int_{t_0}^t H'_{ab}(t')e^{-i\omega_0 t'} \times \left(\int_{t_0}^{t'} H'_{ba}(t'')e^{i\omega_0 t''}\,\mathrm{d}t''\right)\mathrm{d}t'$$

Note that this includes the zeroth order term!

$$c_b^{(2)}(t) = -\frac{i}{\hbar}\int_0^t H'_{ba}(t')e^{i\omega_0 t'}\,\mathrm{d}t'$$

This includes the first order term.

An example of time-dependent perturbation theory is given in the Appendix.

Selection Rules

Suppose we are interested in a system like hydrogen, whose Hamiltonian is spherically symmetric. Then we will specify the state with the usual quantum numbers, n, ℓ and m.

Scalar operators

For any scalar operator $\hat{f}$ it is true that

$$\langle n'\ell'm'|\,\hat{f}\,|n\ell m\rangle = \delta_{\ell\ell'}\delta_{mm'}\left\langle n'\ell\middle\|\hat{f}\middle\|n\ell\right\rangle$$

That is to say that the matrix element is only non-zero when $m = m'$ *and* $\ell = \ell'$. The odd looking matrix element is just a way of saying that it is a constant that depends on n, n' and ℓ, but *not* m.

Vector operators

For the matrix elements

$$\langle n'\ell'm'|\,V_i\,|n\ell m\rangle$$

where $\boldsymbol{V}$ is *any* vector operator and we are looking at the matrix element that takes the i-th component of this operator. We can use the selection rules from chapter 6:

$$\Delta\ell = 0, \pm 1, \quad \text{and} \quad \Delta m = 0, \pm 1$$

What this means is that the matrix element for any of the components of the vector operator is zero, *unless* the conditions in the above equation are met. This tells us that some transitions are forbidden!

Specifically for the matrix elements of the components of

$$\langle n'\ell'm'|\,\boldsymbol{r}\,|n\ell m\rangle$$

These are non-zero iff:

$$\Delta\ell = \pm 1, \quad \text{and} \quad \Delta m = 0, \pm 1$$

The additional constraint, saying that $\Delta\ell$ may not be 0, comes from selection rules due to the parity of the wave functions. For example the transition $|200\rangle \rightsquigarrow |100\rangle$ is *not* allowed for electric dipole transitions, because $\Delta\ell = 0$.

Variational Principle

For *any* normalised state, ψ, it is true that

$$E_{gs} \leq \langle\psi|\,H\,|\psi\rangle = \langle H\rangle$$

This is true because if we write ψ out as a linear combination of H's eigenstates:

$$|\psi\rangle = \sum_n c_n\,|\psi_n\rangle$$

and thus

$$\langle H\rangle = \sum_n |c_n|^2 E_n \geq \sum_n |c_n|^2 E_{gs} = E_{gs}$$

as ψ is normalised. Additionally, if $\langle\psi_{gs}|\psi\rangle = 0$ then

$$\langle H\rangle \geq E_{fe}$$

where E_{fe} is the energy of the first excited state. However, it is not always easy to determine whether $\langle\psi_{gs}|\psi\rangle = 0$.

This principle can be extremely useful, because if you choose a ψ that is *similar* to the real ground state, you will get a very good upper bound for the energy of the ground state. For an example, where the energy of the ground state of a Helium atom is approximated, see the Appendix.

The WKB Approximation

The WKB (Wentzel, Kramers, Brillouin) method can be applied in many different areas of physics, not only quantum mechanics. In fact, it can be applied to any differential equation where the coefficient in front of the highest order differential is very small compared to the other coefficients. The approximation begins by rewriting Schrödinger's equation as:

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\frac{p^2}{\hbar^2}\psi, \quad p(x) \equiv \sqrt{2m(E - V(x))}$$

Next we assume that

$$\psi(x) = A(x)e^{i\phi(x)}$$

implying that Schrödinger's equation can be written as

$$A'' = A\left((\phi')^2 - \frac{p(x)^2}{\hbar^2}\right)$$

and

$$\left(A^2\phi'\right)' = 0$$

This is where the approximation comes. Assume that $A''/A \ll (\phi')^2$ and $A''/A \ll p^2/\hbar^2$, then

$$\frac{\mathrm{d}\phi}{\mathrm{d}x} = \pm\frac{p}{\hbar}$$

and integrating Equation once:

$$A = \frac{C}{\sqrt{|\phi'|}}$$

Thus

$$\psi(x) \approx \frac{C}{\sqrt{p(x)}}e^{\pm\frac{i}{\hbar}\int p(x)\mathrm{d}x}$$

Notice that

$$|\psi|^2 \approx \frac{|C|^2}{p(x)}$$

which bears significant similarity to Heisenberg's uncertainty principle.

Tunneling

In classically forbidden regions, that is regions where $E < V(x)$ the momentum is imaginary, which means that the wave function grows/decays exponentially[‡]:

$$\psi(x) \approx \frac{C}{\sqrt{|p(x)|}}e^{\pm\frac{1}{\hbar}\int |p(x)|\mathrm{d}x}$$

[‡] notice that there is no i in the exponent!

When discussing transmission over a classically forbidden region, we would like to compare the norm of the wave-function to the left of the barrier with the norm of the wave-function to the right of the barrier. Assuming the incident wave is travelling from left to right, and that there is a low percentage of double reflection (very little bit of the wave function is travelling to the left), we can approximate the general solution by a simpler term:

$$\begin{aligned}\psi(x) &\approx \frac{C}{\sqrt{|p(x)|}}e^{\frac{1}{\hbar}\int_0^x |p(x')|\mathrm{d}x'} + \frac{D}{\sqrt{|p(x)|}}e^{-\frac{1}{\hbar}\int_0^x |p(x')|\mathrm{d}x'} \\ &\approx \frac{D}{\sqrt{|p(x)|}}e^{-\frac{1}{\hbar}\int_0^x |p(x')|\mathrm{d}x'}\end{aligned}$$

where we have put the left barrier at $x = 0$. Note that the right barrier is at $x = a$, as in the book, on page 359.

Then the relative amplitudes of the incident and transmitted waves is *proportional to*

$$\frac{|\psi(a)|}{|\psi(0)|} \sim e^{-\frac{1}{\hbar}\int_0^a |p(x')|\mathrm{d}x'}$$

Thus

$$T = \frac{|\psi(a)|^2}{|\psi(0)|^2} \sim e^{-2\gamma}, \quad \gamma \equiv \frac{1}{\hbar}\int_0^a |p(x)|\,\mathrm{d}x$$

Note the looseness of $\sim$. This is due to the fact that there is a missing constant, which is

$$\sqrt{\left|\frac{p(a)}{p(0)}\right|}$$

An example is given in the Appendix, where we approximate the lifetime of nuclei that undergo α-decay.

Some things no one can remember

Generally when dealing with spin the following is true

$$\begin{aligned} S_\pm = S_x \pm iS_y \quad &\Leftrightarrow \quad S_x = \frac{1}{2}\left(S_+ + S_-\right) \\ &\qquad\; S_y = \frac{1}{2i}(S_+ - S_-) \\ S^2\left|s\,m\right\rangle &= \hbar^2 s(s+1)\left|s\,m\right\rangle \\ S_z\left|s\,m\right\rangle &= \hbar m\left|s\,m\right\rangle \\ s &= \frac{1}{2}n, \quad \text{for} \quad n \in \mathbb{N} \\ m &= -s, -s+1, ..., s-1, s \end{aligned}$$

When dealing with **spin-half** systems, we use the **Pauli matrices**:

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

These matrices are expressed in the basis of $|\uparrow\rangle_z$ and $|\downarrow\rangle_z$, that is the spin-states that point parallel and anti-parallel to the z-axis. For example these matrices tell us what the S_x, S_y and S_z operators do on states that are expressed in terms of $|\uparrow\rangle_z$ and $|\downarrow\rangle_z$, as

$$S_i = \frac{\hbar}{2}\sigma_i, \quad i \in \{x, y, z\}$$

it can also be beneficial to know what S_+ and S_- are, expressed in this basis

$$S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

When dealing with **spin-one** systems we can do a similar trick, except that the matrices are 3×3, as there are three states ($m \in \{-1, 0, 1\}$). Once again we can define the raising and lowering operators:

$$S_+ = \sqrt{2}\hbar \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}, \quad S_- = \sqrt{2}\hbar \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$$

and with these the three matrices

$$S_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$
$$S_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}$$
$$S_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

once again, this is expressed in the basis of z, thus in the basis $\{|1\rangle_z, |0\rangle_z, |-1\rangle_z\}$.

APPENDIX

Fixing the Hydrogen atom

Due to coupling between the spin of the electron, the angular momentum of the electron and the spin of the proton (due to electromagnetic interactions) the Hamiltonian is not quite as simple as what we used in QM1. Instead the resulting Hamiltonian is the old Hamiltonian plus some small perturbation.

We split these corrections up into the following terms:

1. Bohr energies (the energies from QM1)
2. Fine structure (relativistic effect and spin-orbit coupling)
3. Lamb shift (due to the quantisation of the electric field)
4. Hyperfine structure (interaction between the magnetic dipole moments of the electron and proton)

These effects' order of magnitude is described using the *fine structure* constant:

$$\alpha \equiv \frac{e^2}{4\pi\varepsilon_0\hbar c} \approx \frac{1}{137.036}$$

In which case the orders of magnitude of the effects are given by

Effect	Order
Bohr energies	$\alpha^2 m_e c^2$
Fine structure	$\alpha^4 m_e c^2$
Lamb Shift	$\alpha^5 m_e c^2$
Hyperfine splitting	$(m_e/m_p)\alpha^4 m_e c^2$

Fine Structure:

The fine structure of hydrogen is due to two separate effects: a **relativistic correction** and **spin-orbit coupling**.

The relativistic correction is due to the relativistic kinetic energy being:

$$T = \frac{mc^2}{\sqrt{1-(v/c)^2}} - mc^2$$

The resulting first order correction to the n-th energy is:

$$E_n^{(1)} = -\frac{\left(E_n^{(0)}\right)^2}{2mc^2}\left(\frac{4n}{\ell+1/2}-3\right)$$

Spin-orbit coupling is due to the fact that the electron sees the proton as a moving charge, which induces a magnetic field. This magnetic field exerts a torque on the electron, tending to align the magnetic moment of the electron with the magnetic field. The Hamiltonian can be written as

$$H = -\boldsymbol{\mu}\cdot\boldsymbol{B} = \left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{1}{m^2c^2r^3}\boldsymbol{S}\cdot\boldsymbol{L}$$

In order to solve this, we defined the total angular momentum:

$$\boldsymbol{J} \equiv \boldsymbol{L} + \boldsymbol{S}$$

because this allowed us to express $\boldsymbol{S}\cdot\boldsymbol{L}$ as

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

Which gave us the first order correction to the energy:

$$E_{nj}^{(1)} = -\frac{E_n^{(0)}\alpha^2}{n^2}\left(\frac{n}{j+1/2}-\frac{3}{4}\right)$$

Note that $|\ell - s| \le j \le \ell + s$.

Zeeman Effect

The Zeeman effect is due to an external magnetic field, and is therefore split up into three domains, weak-field, intermediate-field and strong-field Zeeman effect. But generally the Zeeman effect is due to a coupling between the spin of the electron to the external magnetic field, and the angular momentum of the electron coupling to the external magnetic field. The Hamiltonian for this system is

$$H_Z' = \frac{e}{2m}\left(\boldsymbol{L}+2\boldsymbol{S}\right)\cdot\boldsymbol{B}_{ext}$$

1. **Weak-Field Zeeman Effect:** $B_{ext} \ll B_{int}$, which means the fine structure dominates. Therefore we can treat $H_{Bohr} + H_{fs}'$ as the unperturbed Hamiltonian, and H_Z' as the perturbation. The first order correction in this regime is

   $$E_Z^{(1)} = \frac{e}{2m}B_{ext}\hat{\boldsymbol{z}}\cdot\langle\boldsymbol{L}+2\boldsymbol{S}\rangle$$

   This can be written using the Landé g-factor:

   $$E_Z^{(1)} = \mu_B g_J B_{ext} m_j$$

   where

   $$g_J = 1 + \frac{j(j+1)-\ell(\ell+1)+s(s+1)}{2j(j+1)}$$

   and the Bohr magneton, μ_B is

   $$\mu_B = \frac{e\hbar}{2m} = 5.788\times10^{-5}\frac{\text{eV}}{\text{T}}$$

2. **Intermediate-Field Zeeman Effect:** $B_{ext} \approx B_{int}$, therefore the effects from fine structure are approximately of the same magnitude as those from the Zeeman effect, therefore the unperturbed Hamiltonian is that of the Hydrogen atom, and the perturbation is

   $$H' = H_Z' + H_{fs}'$$

   See page 309 and 310 in the book for a calculation of the first order correction to the energy of hydrogen atoms in the first excited state.

3. **Strong-Field Zeeman Effect:** $B_{ext} \gg B_{int}$, thus the Zeeman effect dominates over the fine structure. The Hamiltonian for this is

   $$H = H_{Bohr} + \frac{e}{2m}B_{ext}(L_z + 2S_z)$$

   We know that $[H, L_z] = [H, S_z] = 0$, thus

   $$E_{nmm_\ell m_s} = E_n^{(0)} + \mu_B B_{ext}(m_\ell + 2m_s)$$

   And now the fine structure must be treated as a perturbation to the Hamiltonian, and the first order correction is

   $$E_{fs}^{(1)} = \frac{13.6\text{eV}}{n^3}\alpha^2\left(\frac{3}{4n} - \left(\frac{\ell(\ell+1)-m_\ell m_s}{\ell(\ell+1/2)(\ell+1)}\right)\right)$$

Hyperfine Splitting

The proton constitutes a magnetic moment, though its moment is far weaker than the electron's (the magnetic moment is inversely proportional to the mass):

$$\boldsymbol{\mu}_p = \frac{g_p e}{2m_p}\boldsymbol{S}_p, \quad \boldsymbol{\mu}_e = -\frac{e}{m_e}\boldsymbol{S}_e$$

Thus the Hamiltonian of the electron in the magnetic field due to the proton's magnetic dipole moment is

$$H_{hf}' = \frac{\mu_0 g_p e^2}{m_p m_e}\left(\frac{3(\boldsymbol{S}_p\cdot\hat{\boldsymbol{r}})(\boldsymbol{S}_e\cdot\hat{\boldsymbol{r}}) - \boldsymbol{S}_p\cdot\boldsymbol{S}_e}{8\pi r^3} + \frac{\boldsymbol{S}_p\cdot\boldsymbol{S}_e\delta^3(\boldsymbol{r})}{3}\right)$$

This leads to the following first order correction to the energy of the ground state of hydrogen:

$$E_{hf}^{(1)} = \frac{4g_p\hbar^4}{3m_p m_e^2 c^2 a^4} \begin{cases} +\frac{1}{4}, & \text{(triplet)} \\ -\frac{3}{4}, & \text{(singlet)} \end{cases}$$

The singlet and triplet are due to how spins are added. For more details on this, see Example 4.5 in the book (page 176).

Sinusoidal Perturbations

Suppose the perturbation has a periodic time dependence:

$$H'(\boldsymbol{r}, t) = V(\boldsymbol{r})\cos(\omega t)$$

Then

$$H'_{ab} = V_{ab}\cos(\omega t), \quad V_{ab} \equiv \langle\psi_a| V |\psi_b\rangle$$

We assume that we begin in the state $\Psi(t=0) = \psi_a$, then to first order we have

$$\begin{aligned} c_b^{(1)}(t) &= -\frac{i}{\hbar}V_{ba}\int_0^t \cos(\omega t')e^{i\omega_0 t'}\,\mathrm{d}t' \\ &= -\frac{V_{ba}}{2\hbar}\left(\frac{e^{i(\omega_0+\omega)t}-1}{\omega_0+\omega} + \frac{e^{i(\omega_0-\omega)t}-1}{\omega_0-\omega}\right) \end{aligned}$$

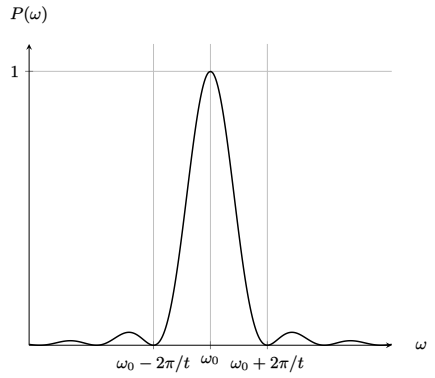
However, we are often interested in the regime where $\omega_0 \approx \omega$, where it is true that

$$\omega + \omega_0 \gg |\omega_0 - \omega|$$

Thus we can ignore the term where the frequencies are added. This gives us the following transition probability

$$P_{a\to b}^{(1)}(t) = |c_b^{(1)}(t)|^2 = \frac{|V_{ab}|^2}{\hbar^2}\frac{\sin^2\left(\frac{(\omega_0-\omega)t}{2}\right)}{(\omega_0-\omega)^2}$$

This gives us a probability that oscillates between 0 and $|V_{ab}|^2/(\hbar^2(\omega_0-\omega)^2)$. Here is a plot of the amplitude of this oscillation as a function of ω:



Figur 1

Spontaneous Emission

Let us picture a system that starts with N_a atoms in the lower energy state, ψ_a, and N_b in the higher energy state, ψ_b.

We wish to describe how N_a and N_b change, as a function of time:

$$\frac{\mathrm{d}N_b}{\mathrm{d}t} = -N_b A - N_b B_{ba}\rho(\omega_0) + N_a B_{ab}\rho(\omega_0)$$

where A is the spontaneous decay/emission rate. B_{ab} is the rate at which stimulated excitation/absorption occurs and B_{ba} is the rate at which stimulated decay/emission occurs. Assuming the system is in equilibrium the $\dot{N}_b = 0$, thus

$$\rho(\omega_0) = \frac{A}{(N_a/N_b)B_{ab} - B_{ba}} = \frac{A}{e^{\hbar\omega_0/k_BT}B_{ab} - B_{ba}}$$

where the last equality is due to the **Boltzmann distribution** from thermodynamics. However, we know from Planck's blackbody formula that

$$\rho(\omega) = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\hbar\omega/k_BT}-1}$$

Thus we conclude that

$$B_{ba} = B_{ab}, \quad A = \frac{\omega^3\hbar}{\pi^2 c^3}B_{ba}$$

It can be shown that the stimulated rate of emission due to incoherent, unpolarised light incident from all directions is

$$R_{b\to a} = \frac{\pi}{3\varepsilon_0\hbar^2}\,|\boldsymbol{\wp}|^2\,\rho(\omega_0), \quad \boldsymbol{\wp} \equiv -e\,\langle\psi_b|\,\boldsymbol{r}\,|\psi_a\rangle$$

thus

$$A = \frac{\omega_0^3|\boldsymbol{\wp}|^2}{3\pi\varepsilon_0\hbar c^3}$$

The Ground State of Helium

The Hamiltonian for a helium atom (ignoring fine structure and smaller corrections):

$$H = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}\right)$$

and the experimental value for the energy of the ground state is

$$E_{gs} = -78.975\text{eV}$$

If we ignore the term that includes both $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ we can treat the Hamiltonian as two separable hydrogen atoms (with some extra factors) and the energy would be $-109\,\mathrm{eV} = 8E_1$. Thus the term we left out is important if we want a better estimate. Let's use the separable solution as the variational wave-function:

$$\psi_0(\boldsymbol{r}_1, \boldsymbol{r}_2) = \psi_{100}(\boldsymbol{r}_1)\psi_{100}(\boldsymbol{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a}$$

Thus the missing term is

$$\langle V_{ee} \rangle = \left(\frac{e^2}{4\pi\varepsilon_0}\right)\left(\frac{8}{\pi a^3}\right)^2 \iint \mathrm{d}^3\boldsymbol{r}_1 \mathrm{d}^3\boldsymbol{r}_2 \, \frac{e^{-4(r_1+r_2)/a}}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}$$

This integral can be solved using spherical coordinates, and the value of $\langle V_{ee} \rangle$ is:

$$\langle V_{ee} \rangle = 34\mathrm{eV}$$

which puts the ground state energy at $E_{gs} \approx -75\,\mathrm{eV}$. This is close, but by adding another parameter, the effective charge of the nucleus, Z, we can do even better. The electrons can diminish the effective charge of the nucleus, therefore we expect that the effective charge will be somewhere between 1 and 2. Thus we would like to use this wave-function:

$$\psi_1(\boldsymbol{r}_1, \boldsymbol{r}_2) \equiv \frac{Z^3}{\pi a^3} e^{-Z(r_1+r_2)/a}$$

Usually the variational principle doesn't touch the Hamiltonian; however, we can always add and subtract things, leaving the Hamiltonian unchanged. This will help us motivate our choice of ψ_1. The rewritten Hamiltonian is

$$\begin{aligned} H = &-\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right) \\ &+ \frac{e^2}{4\pi\varepsilon_0}\left(\frac{Z-2}{r_1} + \frac{Z-2}{r_2} + \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}\right) \end{aligned}$$

Which yields the following energy:

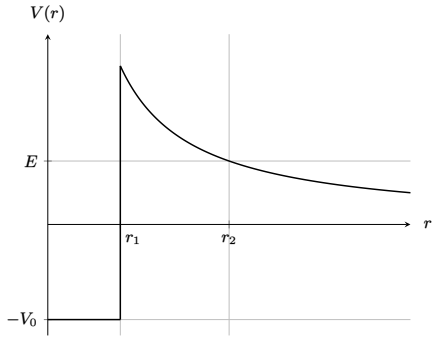
$$\langle H \rangle = \left(-2Z^2 + \frac{27}{4}Z\right) E_1$$

where E_1 is the ground state energy of the hydrogen atom. Now we can minimise the polynomial in Z, which reaches a minimum at $Z = 1.6875$, which puts our estimate of the ground state energy of a helium atom at

$$\langle H \rangle = -77.5\mathrm{eV}$$

Gamow's theory of α-decay

Consider the following graph, that depicts the potential due to the strong nuclear force, together with the electric force, that an α-particle experiences while in the vicinity of a nucleus:



Figur 2

Thus we are interested in the region between r_1 and r_2 as this is the classically forbidden region. We can determine the value of r_2 from the (known) value of E, using the function of the potential:

$$\frac{1}{4\pi\varepsilon_0}\frac{2Ze^2}{r_2} = E$$

Once that is done, all that is left is plugging in. The resulting expression is

$$\begin{aligned} \gamma &= \frac{\sqrt{2mE}}{\hbar}\left(r_2\left(\frac{\pi}{2} - \sin^{-1}\sqrt{\frac{r_1}{r_2}}\right) - \sqrt{r_1(r_2 - r_1)}\right) \\ &\approx \frac{\sqrt{2mE}}{\hbar}\left(\frac{\pi}{2}r_2 - 2\sqrt{r_1 r_2}\right) \end{aligned}$$

Now this tells us something about T, which is the probability of transmission. Now we want to determine the probability of transmission per unit time, which raises the question: how many times does the particle "hit"the wall per unit of time? Well, we can relate this to the velocity of the particle that we measure once the particle has left the nucleus, v, and to the radius r_1. Note that the particle has to travel $2r_1$ to go from one wall to the other, thus the probability of decay per unit time is

$$\frac{v}{2r_1}e^{-2\gamma}$$

which implies the **lifetime** of this nucleus is:

$$\tau = \frac{2r_1}{v}e^{2\gamma}, \quad \gamma \approx \frac{\sqrt{2mE}}{\hbar}\left(\frac{\pi}{2}r_2 - 2\sqrt{r_1 r_2}\right)$$