FURTHER QUANTUM MECHANICS

Part 1: Pertubation Theory

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What is a perturbation?

A 'small' change H_1 to the Hamiltonian of a solved problem H_0.

Notation: Perturbed problem $H\left|n\right\rangle = E_n\left|n\right\rangle$

But $H = H_0 + H_1$ and the unperturbed problem is solved: $H_0\left|n_0\right\rangle = E_n^{(0)}\left|n_0\right\rangle$.

When is a perturbation small?

The fundamental assumption of perturbation theory: The unperturbed ket is a good approximation to the exact ket. The unperturbed kets form a complete set so we can write

$$\left|n\right\rangle = \sum_m c_m\left|m_0\right\rangle \qquad \text{where} \quad \sum_m |c_m|^2 = 1.$$

The fundamental assumption means then implies:

there is one big term in this expansion: $c_n \approx 1$ *and all other terms are small:* $c_m \ll 1$ *for* $n \neq m$*.*

If we don't care about normalisation (we can always normalise at the end of the calculation, and it doesn't affect eigenvalues) then we can in fact divide by c_n and define instead

$$\left|n\right\rangle = \left|n_0\right\rangle + \sum_{m\neq n} c_m\left|m_0\right\rangle.$$

The correction to the ket is orthogonal to the unperturbed ket.

Perturbation Parameters

In perturbation theory there is usually an identifiable physical parameter λ such that $H_1 = \lambda h_1$. For example, a fruitful source of perturbation problems is application of external fields to atoms. These give perturbations like $q\phi = -qEz$ and $-\mathbf{B} \cdot \boldsymbol{\mu}$ where q is the electric charge, and $\boldsymbol{\mu}$ the magnetic dipole moment. Obviously the external field strengths E and B can play the role of λ.

We can now attempt an expansion of the unknown ket and eigenvalue as a power series in λ:

$$E_n = \sum_p \lambda^p e_n^{(p)} = e_n^{(0)} + \lambda e_n^{(1)} \ldots = E_n^{(0)} + E_n^{(1)} \ldots$$

where the first term is independent of the perturbation, the second term scales linearly with the perturbation, and so on. In effect we are splitting up the corrections to the eigenvalue and ket into parts that vary as different powers of λ:

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} \ldots \qquad |n\rangle = |n_0\rangle + |n_1\rangle + |n_2\rangle + \ldots$$

where $E_n^{(2)}$ contains a factor λ^2 and $|n_1\rangle$ a factor of λ etc.

The question of the convergence of these series is a delicate one (and depends on the problem). But even if the series don't converge, we can still use the first few terms to improve our approximate zeroth order solution.

Non-degenerate Perturbation Theory

We first apply this approach to a non-degenerate level, so that there is a single zeroth-order ket $|n_0\rangle$ with eigenvalue $E_n^{(0)}$. We write down the Schrodinger equation:

$$(H_0 + H_1)\left[|n_0\rangle + |n_1\rangle + |n_2\rangle\right] = (E_n^{(0)} + E_n^{(1)} + E_n^{(2)})\left[|n_0\rangle + |n_1\rangle + |n_2\rangle\right]$$

and identify zeroth-, first-, second-order terms from the number of factors of λ, and equate them separately:

Zeroth Order: $H_0\,|n_0\rangle = E_n^{(0)}\,|n_0\rangle$

First Order: $H_1\,|n_0\rangle + H_0\,|n_1\rangle = E_n^{(1)}\,|n_0\rangle + E_n^{(0)}\,|n_1\rangle$

Second Order: $H_1\,|n_1\rangle + H_0\,|n_2\rangle = E_n^{(2)}\,|n_0\rangle + E_n^{(1)}\,|n_1\rangle + E_n^{(0)}\,|n_2\rangle$

We recognise the unperturbed equation, giving us the $E_n^{(0)}$ and $|n_0\rangle$ we already know. The other equations give us the corrections.

First-Order Correction to Energy

The first-order equation contains two things we don't know, the correction to the ket $|n_1\rangle$, and the correction to the energy $E_n^{(1)}$:

$$H_1 |n_0\rangle + H_0 |n_1\rangle = E_n^{(1)} |n_0\rangle + E_n^{(0)} |n_1\rangle \,.$$

We can isolate these by taking the inner product with one of the unperturbed kets:

Suppose we take the inner product with $|n_0\rangle$:

$$\langle n_0| H_1 |n_0\rangle + \langle n_0| H_0 |n_1\rangle = E_n^{(1)} \langle n_0| n_0\rangle + E_n^{(0)} \langle n_0| n_1\rangle \,.$$

But on the left we can use the Hermitian property of H_0:

$$\langle n_0| H_0 |n_1\rangle = \Big(\langle n_1| H_0 |n_0\rangle\Big)^* = \Big(E_n^{(0)} \langle n_1| n_0\rangle\Big)^* = E_n^{(0)} \langle n_0| n_1\rangle$$

which cancels a term on the right. (In fact, both of these terms are zero since $\langle n_0| n_1\rangle = 0$.)

First-Order Correction to Energy

This leaves just two terms which we can immediately rearrange to give

$$\boxed{E_n^{(1)} = \frac{\langle n_0 | H_1 | n_0 \rangle}{\langle n_0 | n_0 \rangle} = \langle n_0 | H_1 | n_0 \rangle}$$

since the denominator is 1. (But note we don't have to do perturbation theory with normalised kets — and if we don't, then the theory still gives the correct result.)

The first-order energy correction is the expectation of the perturbation in the unperturbed state.

First-Order Correction to ket

The correction to the ket $|n_1\rangle$ is found by taking the inner product with any other unperturbed ket $|m_0\rangle$:

$$\langle m_0| H_1 |n_0\rangle + \langle m_0| H_0 |n_1\rangle = E_n^{(1)} \langle m_0| n_0\rangle + E_n^{(0)} \langle m_0| n_1\rangle .$$

The term involving $E_n^{(1)}$ vanishes and the second term on the left becomes (same argument) $E_m^{(0)} \langle m_0| n_1\rangle$. Thus

$$\boxed{\langle m_0| n_1\rangle = \frac{\langle m_0| H_1 |n_0\rangle}{E_n^{(0)} - E_m^{(0)}} \quad m \neq n}$$

This defines all the amplitudes for $|n_1\rangle$ except $\langle n_0| n_1\rangle$. But that is just zero because they are orthogonal. So

$$\boxed{|n_1\rangle = \sum_{m\neq n} \frac{|m_0\rangle \langle m_0| H_1 |n_0\rangle}{E_n^{(0)} - E_m^{(0)}}}$$

Reflections on First-Order Results

(1) That the energy correction is just the expectation is *unforgettable* — what else could it be? How else do you get a number out of an operator (H_1) and a ket ($|n_0\rangle$)? (The answer of course is an eigenvalue, but that's exactly what we trying to avoid!) The result is much more memorable than its derivation.

(2) To look at it another way, eigenvalues are special cases of expectation values:

$$H\,|n\rangle = E_n\,|n\rangle \quad \rightarrow \quad \langle n|\,H\,|n\rangle = E_n = \langle n|\,H_0\,|n\rangle + \langle n|\,H_1\,|n\rangle$$

If we make the fundamental assumption that the unperturbed ket is a good approximation to the exact ket we immediately get the same result $E_n \approx E_n^{(0)} + \langle n_0|\,H_1\,|n_0\rangle$.

(3) If we rearrange the first-order equation we find out why we don't determine $\langle\, n_0|\, n_1\rangle$:

$$H_0\,|n_1\rangle - E_n^{(0)}\,|n_1\rangle = -\left(H_1 - E_n^{(1)}\right)|n_0\rangle$$

The corresponding Schrodinger equation is a linear differential equation with an inhomogeneous term. The solution we have found is the particular integral, but we can add any multiple of the complementary function, which is $|n_0\rangle$!

Second-Order Correction to Energy

We only find the second-order correction to the energy, not the ket. This is because we are usually more interested in eigenvalues than kets, and in general a p'th-order wavefunction enables us to find an eigenvalue correct to order $2p+1$. (So the first-order ket gives us the third-order energy as well . . .)

$$H_1 |n_1\rangle + H_0 |n_2\rangle = E_n^{(2)} |n_0\rangle + E_n^{(1)} |n_1\rangle + E_n^{(0)} |n_2\rangle$$

As before there are two things we don't know, $E_n^{(2)}$ and $|n_2\rangle$.
And as before we can eliminate all the unknown kets by taking the inner product with $|n_0\rangle$:

$$\boxed{E_n^{(2)} = \langle n_0| H_1 |n_1\rangle}$$

We can of course substitute for $|n_1\rangle$:

$$\boxed{E_n^{(2)} = \sum_{m\neq n} \frac{\langle n_0| H_1 |m_0\rangle \langle m_0| H_1 |n_0\rangle}{E_n^{(0)} - E_m^{(0)}} = \sum_{m\neq n} \frac{|\langle m_0| H_1 |n_0\rangle|^2}{E_n^{(0)} - E_m^{(0)}}}$$

Second-Order Correction to Energy

(Alternatively we could eliminate the H_1 matrix elements to get

$$E_n^{(2)} = \sum_{m \neq n} \left(E_n^{(0)} - E_m^{(0)} \right) |\langle m_0 | n_1 \rangle|^2$$

but this is by no means a normal move!)

These equations indicate the close link between the first-order correction to the ket and the second-order correction to the energy: you can't have one without the other! The first form shows that if $|n_1\rangle = 0$ then so is $E_n^{(2)}$. The final form shows that $E_n^{(2)}$ could only be zero by some flukey cancellation in the sum over amplitudes.

There is an interesting symmetry of the mixing amplitudes $\langle m_0 | n_1 \rangle$: $\langle m_0 | n_1 \rangle = -\langle n_0 | m_1 \rangle^*$. Thus if a bit of state m is mixed into n by the perturbation then there is an equal but opposite mixing of n into m. This is exactly what we need to preserve orthogonality to first order.

Then we see that states that mix in first order repel in second order. And hence the second-order correction to the ground state is always negative.

Example 1: Box with a non-flat bottom

For our first example we take the particle in a box (between 0 and a) with a perturbation:

$$H_1 = W \cos\left[\frac{2\pi x}{a}\right].$$

The unperturbed eigenvalues are $E_n^{(0)} = \dfrac{n^2\pi^2\hbar^2}{2ma^2} = n^2 E_1$ (where $n = 1, 2, 3\ldots$)

and the eigenkets have a simple x-representation $\langle x|\, n_0\rangle = u_n(x) = \sqrt{\dfrac{2}{a}}\sin\left[\dfrac{n\pi x}{a}\right]$.
The first-order energy shift is then

$$E_n^{(1)} = \langle n_0|\, H_1\, |n_0\rangle = \int_0^a u_n(x)\, H_1\, u_n(x)\, dx$$

The integral is helped by the use of an addition formula:

$$H_1 u_n(x) = \sqrt{\frac{2}{a}} W \cos\left[\frac{2\pi x}{a}\right]\sin\left[\frac{n\pi x}{a}\right] = \frac{W}{2}\sqrt{\frac{2}{a}}\left[\sin\left(\frac{(n+2)\pi x}{a}\right) + \sin\left(\frac{(n-2)\pi x}{a}\right)\right].$$

This simplifies to $\frac{W}{2}(u_{n+2} - u_{n-2})$ except for the special cases of $n = 1$ and $n = 2$. For $n = 2$, $\sin(n-2)\pi x/a = 0$ while for $n = 1$ $\sin(n-2)\pi x/a = -\sin\pi x/a$.

Example 1: Box with a non-flat bottom

We can summarise the action of H_1 on the eigenkets as follows:

$$H_1 \left| n_0 \right\rangle = \begin{cases} \frac{W}{2}\Big(\left|(n+2)_0\right\rangle + \left|(n-2)_0\right\rangle \Big) & \text{for } n > 2 \\ \frac{W}{2} \left|4_0\right\rangle & \text{for } n = 2 \\ \frac{W}{2}\Big(\left|3_0\right\rangle - \left|1_0\right\rangle \Big) & \text{for } n = 1 \end{cases}$$

Thus almost all the $E_n^{(1)}$ vanish because $H_1 \left| n_0 \right\rangle$ is orthogonal to $\left| n_0 \right\rangle$. The only exception is

$$E_1^{(1)} = \left\langle 1_0 \right| H_1 \left| 1_0 \right\rangle = \frac{W}{2}\Big(\left\langle 1_0 \middle| 3_0 \right\rangle - \left\langle 1_0 \middle| 1_0 \right\rangle \Big) = -\frac{W}{2}$$

This also gives us all the matrix elements of H_1 to evaluate the ket correction:

$$\left| n_1 \right\rangle = \frac{W}{2}\left[\frac{\left|(n-2)_0\right\rangle}{[n^2-(n-2)^2]E_1} + \frac{\left|(n+2)_0\right\rangle}{[n^2-(n+2)^2]E_1} \right] \qquad \text{(only 1 term for } n\text{=1,2)}$$

Finally this allows us to calculate the second-order correction to the energy:

$$E_n^{(2)} = \frac{W^2}{4}\left[\frac{1}{[n^2-(n-2)^2]E_1} + \frac{1}{[n^2-(n+2)^2]E_1}\right] \qquad \text{(only 1 term for } n\text{=1,2)}$$

For example $E_1^{(2)} = \frac{W^2}{4}\left[\frac{-1}{8E_1}\right]$ and $E_3^{(2)} = \frac{W^2}{4}\left[\frac{1}{8E_1} - \frac{1}{16E_1}\right]$.

This problem can be solved exactly - the Schrodinger equation becomes the Mathieu equation, and the wavefunctions are Mathieu functions. There is a Mathematica notebook on the FQM Website which compares the exact and perturbative solutions.

Example 2: Quadratic Stark Effect in Hydrogen

The Stark effect is a perturbation by an electric field $\mathbf{E} = -\nabla\Phi$. There are two charges in the atom, so the change in the Hamiltonian is $H_1 = +e\Phi(0) - e\Phi(\mathbf{r})$.

For a uniform $\mathbf{E}$ in the z-direction, magnitude $\mathcal{E}$, $\Phi(\mathbf{r}) = \Phi(0) - \mathcal{E}z$ so $H_1 = e\mathcal{E}z$.

This Hamiltonian has a useful commutator with the Parity operator P.

$[H_0, P] = 0$, so the hydrogen eigenkets can be chosen to be eigenkets of P.

(And these are the $|n\ell m\rangle$ kets.)

But $PH_1 = -H_1 P$, so H_1 *anti*-commutes with P: $PH_1 + H_1 P = 0$.

Consider a matrix element between two parity eigenstates ($p = \pm 1$):

$$\langle n'\ell'm'p'|\, PH_1 + H_1 P \,|n\ell mp\rangle = (p + p')\,\langle n'\ell'm'p'|\, H_1 \,|n\ell mp\rangle = 0$$

So either $p = -p'$, the states have opposite parity, or the matrix element is zero.

Thus all diagonal matrix elements vanish and so does the first-order energy (unless there is degeneracy). (This argument is perfectly general and applies to all atomic states — the Stark effect is usually only second-order.) But in Hydrogen there is degeneracy. . . .

But in the non-degenerate ground state:

$$\boxed{E_1^{(2)} = \sum_{n'\ell' \neq 10} \frac{|\,\langle n'\ell'0|\, e\mathcal{E}z \,|100\rangle\,|^2}{E_1^{(0)} - E_n^{(0)}}.}$$

Example of Degeneracy: Rigid Rotor

This is a system with moment of inertia I free to rotate about an axis.

The Hamiltonian is thus $H_0 = \dfrac{L^2}{2I}$.

The energy levels are $E_n^{(0)} = \dfrac{n^2\hbar^2}{2I}$.

The ground state is non-degenerate: $\langle \phi | 0_0 \rangle = \dfrac{1}{\sqrt{2\pi}}$

But all the excited states are two-fold degenerate, so any basis eigenkets represent an arbitrary choice. Two obvious choices are:

c,s basis:

$$\langle \phi | (1,c)_0 \rangle = \frac{1}{\sqrt{\pi}} \cos\phi$$

$$\langle \phi | (1,s)_0 \rangle = \frac{1}{\sqrt{\pi}} \sin\phi$$

+,− basis:

$$\langle \phi | (1,+)_0 \rangle = \frac{1}{\sqrt{2\pi}} \exp(+\mathrm{i}\phi)$$

$$\langle \phi | (1,-)_0 \rangle = \frac{1}{\sqrt{2\pi}} \exp(-\mathrm{i}\phi)$$

but *any* linear combination of the degenerate eigenkets is an eigenket.

This means the fundamental assumption is no longer necessarily true!

In general a perturbation will remove the degeneracy in E_n. Imagine what happens if we could control the pertubation parameter and make it smaller. As the states approach each other they are each some particular linear combination of our arbitrary basis — *but we don't know what it is.*

So the correct zeroth-order wavefunctions $|(n,z)_0\rangle$ are an unknown linear combination of our original, arbitrary basis $|(n,a)_0\rangle$:

$$|(n,z)_0\rangle = \sum_a |(n,a)_0\rangle \langle (n,a)_0| (n,z)_0\rangle \,.$$

We can now put this (correct but as yet unknown!) ket into the first-order equation:

$$H_1 |(n,z)_0\rangle + H_0 |(n,z)_1\rangle = E^{(1)}_{nz} |(n,z)_0\rangle + E^{(0)}_n |(n,z)_1\rangle$$

We take the inner product with one of our arbitrary basis kets for E_n:

$$\langle (n,a)_0| H_1 |(n,z)_0\rangle + \langle (n,a)_0| H_0 |(n,z)_1\rangle = E^{(1)}_{nz} \langle (n,a)_0| (n,z)_0\rangle + E^{(0)}_n \langle (n,a)_0| (n,z)_1\rangle$$

Two terms cancel in the same way as the non-degenerate case.

This leaves just

$$\langle (n,a)_0 | H_1 | (n,z)_0 \rangle = E^{(1)}_{nz} \langle (n,a)_0 | (n,z)_0 \rangle$$

We simply insert the summation for the unknown state:

$$\sum_{a'} \langle (n,a)_0 | H_1 | (n,a')_0 \rangle \langle (n,a')_0 | (n,z)_0 \rangle = E^{(1)}_{nz} \langle (n,a)_0 | (n,z)_0 \rangle .$$

We have as many equations like this as the order of the degeneracy.

Remembering that $\langle (n,a)_0 | (n,z)_0 \rangle$ are elements of a vector, and $\langle (n,a)_0 | H_1 | (n,a')_0 \rangle$ elements of a matrix, we can write:

$$\boxed{\mathbf{H}_1 \mathbf{c}^{(z)} = E^{(1)}_n \mathbf{c}^{(z)}}$$

An eigenvalue equation!! With a Hermitian matrix in the known (but arbitrary) a basis.

This gives us:

Eigenvalues: Each eigenvalue is one of the first-order energy shifts $E^{(1)}_n$;

Eigenvectors: Each component of the eigenvector gives us one of the amplitudes $\langle (n,a)_0 | (n,z)_0 \rangle$ which define the correct zeroth-order z basis in terms of the a basis.

Again, the result is more memorable than the derivation.

Example: Perturbed Rotor

We perturb the rigid rotor with an angle-dependent potential $V_0 \sin 2\phi$.

We choose the +,− basis and find the shifts in $n = 1$.

The integrals in the matrix elements are of the form

$$\frac{1}{2\pi} \int_0^{2\pi} \left[e^{\pm \mathrm{i}\phi}\right]^* V_0 \left(\frac{e^{\mathrm{i}2\phi} - e^{-\mathrm{i}2\phi}}{2\mathrm{i}}\right) e^{\pm \mathrm{i}\phi}\, d\phi$$

This gives

$$\begin{pmatrix} 0 & -\mathrm{i}V_0/2 \\ \mathrm{i}V_0/2 & 0 \end{pmatrix} \begin{pmatrix} c_+ \\ c- \end{pmatrix} = E_1^{(1)} \begin{pmatrix} c_+ \\ c_- \end{pmatrix}$$

We find $E_1^{(1)} = \pm V_0/2$ and eigenvectors

$$+\frac{V_0}{2} : \quad \mathbf{c}^{(+)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \mathrm{i} \end{pmatrix} \qquad -\frac{V_0}{2} : \quad \mathbf{c}^{(-)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -\mathrm{i} \end{pmatrix}$$

Thus the wavefunction for the state shifted *up* in energy is

$$\frac{1}{2\sqrt{\pi}} \left(e^{\mathrm{i}\phi} + \mathrm{i}e^{-\mathrm{i}\phi}\right) = \frac{1+\mathrm{i}}{2\sqrt{\pi}} \Big(\cos\phi + \sin\phi\Big).$$

If we had used these states to start with, the H_1 matrix would have been diagonal, with the eigenvalues as the diagonal elements.

How to avoid Degenerate Perturbation Theory.

It's obvious that, compared with just evaluating an expectation value in the non-degenerate case, Degenerate Perturbation Theory is a *big deal*.

If we knew the correct zeroth-order wavefunctions to start with we would only have to evaluate the expectation values.

Suppose there is an operator S which commutes with both H_0 and H_1. Then it commutes with the exact H, and the exact eigenstates are eigenstates of S. So we just use the mutual eigenbasis of H_0 and S, $|(n,s)_0\rangle$.

In this basis the off-diagonal elements are all zero (as long as the degenerate states have different s eigenvalues):

$$\langle (n,s)_0|\, SH_1 - H_1 S\, |(n,s')_0\rangle = (s-s')\, \langle (n,s)_0|\, H_1\, |(n,s')_0\rangle = 0$$

In the example given the relevant operator is reflection about the line $\phi = \pi/4, 5\pi/4$ so that the correct eigenfunctions are $\cos(\phi - \pi/4)$ and $\sin(\phi - \pi/4)$.

We can make the Hamiltonion time-dependent if we introduce an interaction with a time-varying external field. We shall consider the interaction is weak enough to be treated by perturbation theory:

$$H = H_0 + V(t)$$

where the eigenvalues and eigenkets of H_0 are known.
Suppose we prepare the system in an eigenstate — say the ground state.
And V varies harmonically — say as $\cos\omega t$.
And there's an excited state at an energy E above the ground state.
This is called absorption spectroscopy. What do we expect?

The example suggests that if $E = \hbar\omega$ then the system responds and can end up in the excited state, and if not, not.

So our physical intuition suggests that the result is discontinuous! This is a hint that we need to be a bit careful. The combination of discrete energy levels and perfectly-defined frequencies is obviously a tricky one. We shall proceed with caution!

Basic equations.

The eigenkets of H_0 form a complete set, so we can always expand a state in terms of them. If $V = 0$ then we have seen that the state is in general

$$|\psi(t)\rangle = \sum_n a_n \exp\left(-\mathrm{i}E_n t/\hbar\right)|n\rangle$$

so a sensible place to start is to assume an expansion of this form but allowing a_n to vary with t:

$$|\psi(t)\rangle = \sum_n a_n(t) \exp\left(-\mathrm{i}E_n t/\hbar\right)|n\rangle .$$

Substitute into the time-dependent Schrodinger equation $\mathrm{i}\hbar d/dt\,|\psi(t)\rangle = (H_0 + V)\,|\psi(t)\rangle$:

$$\sum_n \left(\mathrm{i}\hbar\frac{da_n}{dt} + a_n E_n\right)\exp\left(-\mathrm{i}E_n t/\hbar\right)|n\rangle = \sum_n a_n \exp\left(-\mathrm{i}E_n t/\hbar\right)\Big(E_n + V(t)\Big)|n\rangle .$$

As expected, there is a cancellation so that a_n only changes because of V:

$$\sum_n \mathrm{i}\hbar\frac{da_n}{dt}\exp\left(-\mathrm{i}E_n t/\hbar\right)|n\rangle = \sum_n a_n \exp\left(-\mathrm{i}E_n t/\hbar\right)V(t)\,|n\rangle .$$

Take inner product with $|m\rangle$:

$$\mathrm{i}\hbar \frac{da_m}{dt} \exp\left(-\mathrm{i}E_m t/\hbar\right) = \sum_n a_n \exp\left(-\mathrm{i}E_n t/\hbar\right) \langle m| V(t) |n\rangle .$$

or, taking the time-dependence across:

$$\mathrm{i}\hbar \frac{da_m}{dt} = \sum_n a_n \exp\left(\frac{\mathrm{i}(E_m - E_n)t}{\hbar}\right) \langle m| V(t) |n\rangle .$$

which has an obvious vector/matrix shape:

$$\mathrm{i}\hbar \frac{d\mathbf{a}}{dt} = \widetilde{\mathbf{V}}\mathbf{a}$$

where $\widetilde{\mathbf{V}}$ has matrix elements that oscillate due to the energy difference between states as well as due to the time-dependence of $V(t)$:

$$\widetilde{V}_{mn} = \exp\left(\frac{\mathrm{i}(E_m - E_n)t}{\hbar}\right) \langle m| V(t) |n\rangle$$

We haven't so far made any approximations.

If the number of states is finite and fairly small we can solve these coupled linear equations exactly — numerically if necessary.

But in many problems the number of states involved is too large and we must approximate.

Perturbative Expansion.

We expand a_m in powers of the size of $V(t)$:

$$a_m = a_m^{(0)} + a_m^{(1)} + a_m^{(2)} + \ldots \qquad \text{where } a_m^{(0)} \text{ is independent of } V,\ a_m^{(1)} \propto V \text{ etc}$$

Substituting this into the equation we get

$$\mathrm{i}\hbar\left(\frac{da_m^{(0)}}{dt} + \frac{da_m^{(1)}}{dt} + \frac{da_m^{(2)}}{dt} + \ldots\right) = \sum_n \widetilde{V}_{mn}\left(a_n^{(0)} + a_n^{(1)} + a_n^{(2)} + \ldots\right).$$

Equating powers of V we get a series of equations for the rate of change of each coefficient in terms of the next lower coefficient:

$$\boxed{\begin{array}{rlll} \textbf{Zeroth Order:} & \mathrm{i}\hbar\dfrac{da_m^{(0)}}{dt} = 0 & \rightarrow & a_m^{(0)}(t) = a_m^{(0)}(t_0). \\ \textbf{First Order:} & \mathrm{i}\hbar\dfrac{da_m^{(1)}}{dt} = \displaystyle\sum_n \widetilde{V}_{mn} a_n^{(0)} & \rightarrow & a_m^{(1)}(t) = \dfrac{1}{\mathrm{i}\hbar}\displaystyle\sum_n \left[\int_{t_0}^{t} \widetilde{V}_{mn}\,dt'\right] a_n^{(0)} \\ \textbf{Second Order:} & \mathrm{i}\hbar\dfrac{da_m^{(2)}}{dt} = \displaystyle\sum_n \widetilde{V}_{mn} a_n^{(1)} & \rightarrow & a_m^{(2)}(t) = \dfrac{1}{\mathrm{i}\hbar}\displaystyle\sum_n \left[\int_{t_0}^{t} \widetilde{V}_{mn} a_n^{(1)}(t')\,dt'\right] \end{array}}$$

We shall only consider particularly simple cases:

The initial state is simple: $|\psi(t_0)\rangle = |i\rangle$, so $a_i^{(0)} = 1$ and all the other $a^{(0)}$ are 0.

We also ignore the possibility of diagonal matrix elements $\widetilde{V}_{mm} = 0$. (This is quite common in any case for parity reasons).

We work to first order only.

Then at a later time

$$\boxed{a_m^{(1)}(t) = \frac{1}{\mathrm{i}\hbar}\int_{t_0}^{t} \widetilde{V}_{mi}\, dt \quad \text{for } m \neq i \quad \text{and} \quad a_i^{(0)}(t) = a_i^{(0)}(t_0) = 1}$$

Example 1: Turning on a perturbation.

Consider turning on a otherwise time-independent perturbation, $V(t) = \begin{cases} e^{\alpha t} V & \text{for } t < 0 \\ V & \text{for } t > 0 \end{cases}$

We look at the state at $t = 0$:

$$a_m^{(1)}(0) = \frac{\langle m|\, V\, |i\rangle}{\mathrm{i}\hbar}\int_{-\infty}^{0} \exp\left(\frac{\mathrm{i}(E_m - E_i)t}{\hbar}\right) e^{\alpha t}\, dt \quad \rightarrow \quad a_m^{(1)}(0) = \frac{\langle m|\, V\, |i\rangle}{E_i - E_m + \mathrm{i}\hbar\alpha}$$

Sudden and Adiabatic Approximations.

This has two interesting limits:

$\alpha \to \infty$: This corresponds to a very quick ('sudden') turn-on. In this case $a_m^{(1)} \to 0$: the state at $t = 0$ is unchanged from $t = -\infty$ (apart from normal time-evolution of $|i\rangle$).
But after $t = 0$ we have a Hamiltonian $H_0 + V$, so the time evolution after $t = 0$ is in terms of the eigenkets of the new Hamiltonian $|n'\rangle$:

$$|\psi(0)\rangle = \sum_{n'} |n'\rangle \langle n'| i\rangle \quad \text{and so} \quad |\psi(t)\rangle = \sum_{n'} e^{-\mathrm{i}E'_n t/\hbar} |n'\rangle \langle n'| i\rangle$$

$\alpha \to 0$: This corresponds to a very slow turn on, and at $t = 0$ the state is

$$|\psi(0)\rangle = |i\rangle + \sum_{m \neq i} |m\rangle \frac{\langle m| V |i\rangle}{E_i - E_m} = |i'\rangle \quad \text{to first order.}$$

In this case the wavefunction follows the evolving Hamiltonian in the corresponding eigenket.
This is known as the adiabatic approximation, and requires $\hbar\alpha \ll |E_i - E_m|$.

Example 2: Transition due to an Oscillating Perturbation.

We now consider an oscillating perturbation, such as we might get from applying EM radiation to an atom:

$$V = -\mathbf{E}(t) \cdot \mathbf{D} = -2\mathcal{E} D_z \, \cos \omega t$$

where **D** is the electric dipole moment of the atom, and I have made the radiation linearly polarized in the z-direction with amplitude $2\mathcal{E}$.

We can split the cosine up: $\cos \omega t = (1/2)[e^{\mathrm{i}\omega t} + e^{-\mathrm{i}\omega t}]$.

Since the first-order theory is linear in the perturbation we can treat just one term, which we choose to be $e^{-\mathrm{i}\omega t}$:

$$V(t) = -\mathcal{E} D_z e^{-\mathrm{i}\omega t}.$$

Then, if the perturbation is turned on at $t = 0$ when the atom is in state $|i\rangle$, and turned off at t:

$$\begin{aligned} a_m^{(1)}(t) &= \frac{\langle m| - \mathcal{E} D_z \,|i\rangle}{\mathrm{i}\hbar} \int_0^t \exp\left(\frac{\mathrm{i}(E_m - E_i)t'}{\hbar}\right) \exp -\mathrm{i}\omega t' \, dt' \\ &= \langle m| - \mathcal{E} D_z \,|i\rangle \; \frac{\exp\left(\mathrm{i}\,\Delta E\, t/\hbar\right) - 1}{-\Delta E} \quad \text{where } \Delta E = E_m - \hbar\omega - E_i \\ &= \frac{\langle m| - \mathcal{E} D_z \,|i\rangle}{\Delta E/2} \left(-\mathrm{i} \exp\left(\mathrm{i}\,\Delta E\, t/2\hbar\right)\right) \sin\left(\Delta E\, t/2\hbar\right) \end{aligned}$$

The probability of the atom being in state $|m\rangle$ at time t is

$$|a_m(t)|^2 = \frac{4|\langle m|\,\mathcal{E}^2 D_z\,|i\rangle\,|^2}{\Delta E^2}\ \sin^2\left(\frac{\Delta E\,t}{2\hbar}\right)$$

The probability oscillates, and the amplitude of oscillation involves the square of the ratio of the matrix element squared divided by ΔE. This ratio is typically tiny except when $\Delta E \approx 0$.

This has a natural interpretation in terms of the absorption of a quantum of energy $\hbar\omega$ — a photon in the case of light. But it will happen for any oscillating perturbation.

However $\Delta E = E_i + \hbar\omega - E_m$ is the energy imbalance in the process — we have apparently lost/gained an energy of $\pm\Delta E$ — but only for about one half-cycle of the oscillation $2\pi\hbar/\Delta E$. So the energy imbalance is constrained by

$$\Delta E\,\Delta t \sim 2\pi\hbar.$$

This is the process of 'borrowing energy' mentioned in many popular accounts of QM.

If there happens to be a final state $|m\rangle$ exactly on resonance, $\Delta E = 0$, then the amplitude does not oscillate but grows linearly with t:

$$a_m^{(1)}(t) = \frac{\langle m|-\mathcal{E}D_z\,|i\rangle}{\mathrm{i}\hbar}\,t.$$

This is the 'discontinuity' we naively expected.

Continuum States — the Free Particle

For a free particle the Hamiltonian is $H = \hat{p}^2/2m$ and this obviously commutes with $\hat{p}$.
So we can choose the eigenstates to be the eigenkets of $\hat{p}$: $\hat{p}\,|P\rangle = P\,|P\rangle$. Let $\langle x|\,P\rangle = u_P(x)$.

$$-\mathrm{i}\hbar\frac{\partial u_P}{\partial x} = P\,u_P \quad \rightarrow \quad u_P(x) = A\exp[iPx/\hbar]$$

This is the solution for any value of P, so the possible values of momentum are P = anything, with energy eigenvalues $P^2/2m$ — not discrete eigenvalues but a continuous range.
A is a normalisation constant — but the eigenfunctions are not normalisable!
These two problems always occur together: eigenkets belonging to eigenvalues in a continuous range are unnormalisable. The whole set of states are sometimes referred to as the continuum.

The standard normalisation is 'δ-function normalisation': $\langle\,P'|\,P\rangle = \delta(P - P')$; $A = 1/\sqrt{2\pi\hbar}$.

But if we think about the uncertainty principle the situation is obvious: in an eigenket the momentum is sharply defined, $\Delta p = 0$ and so the position uncertainty must be infinite.
In fact the eigenket $|P\rangle$ is physically unrealisable. The same is true of the position eigenket $|X\rangle$. They still form a basis but physical states must be formed by superposition to make a wavepacket.

Example 3: Fermi's Golden Rule

The 'almost discontinuous' result follows from the combination of discrete energy levels and a single frequency perturbation. The theory looks a bit different when the final state belongs to the continuum, because there is always a final state exactly on resonance.

We consider a transition from an initial discrete state $|i\rangle$, energy E_i to a final continuum $|p\rangle$, energy $E(p)$, induced by a perturbation $V(t) = Ve^{-\mathrm{i}\omega t}$.
The first-order amplitude is as above (p42, last line):

$$a_p^{(1)}(t) = \frac{\langle p|\, V\, |i\rangle}{\Delta E/2} \left(-\mathrm{i}\exp\left(\mathrm{i}\,\Delta E\, t/2\hbar\right)\right)\, \sin\left(\Delta E\, t/2\hbar\right)$$

where $\Delta E = E(p) - \hbar\omega - E_i$. These amplitudes define the first-order ($\propto V$) ket correction:

$$|\psi(t)\rangle = |i\rangle \exp(-\mathrm{i}E_i t/\hbar) + \int_0^\infty a_p^{(1)}(t) \exp(-\mathrm{i}E_p t/\hbar)\, |p\rangle\; dp$$

The excitation probability is given by $|a_p^{(1)}|^2$ summed over the final states:

$$\boxed{\int_0^\infty |a_p^{(1)}(t)|^2\, dp = \int_0^\infty \frac{|\langle p|\, V\, |i\rangle|^2 t^2}{\hbar^2}\, \mathrm{sinc}^2(\Delta E\, t/2\hbar)\, dp}$$

where we have introduced the sinc function $\mathrm{sinc}\, x = \sin x/x$.

The sinc function has a peak at $x = 0$, falling to zero at $x = \pm\pi$. Thus for any value of t the sinc function gives particular weight to final states $E(p)$ for which $-2\pi\hbar/t \leq \Delta E \leq 2\pi\hbar/t$. As time goes on this range gets steadily narrower, emphasising states around the energy conserving state $\Delta E = 0$. It makes sense to change variable to the argument of the sinc function:

$$x = (E(p) - E_i - \hbar\omega)t/2\hbar \quad \text{and} \quad dx = \frac{dE(p)}{dp}\frac{t}{2\hbar}\,dp = \frac{t}{2\hbar\rho_f(E(p))}\,dp$$

$\rho_f = dp/dE(p)$ is known as the density of states factor. It is a measure of the 'quantity' of final states per unit energy range. (The lower limit x_{min} is large and negative.)

$$\int_0^\infty |a_p^{(1)}(t)|^2\,dp = \frac{t}{2\hbar}\int_{x_{\mathrm{min}}}^\infty |\langle p|\,V\,|i\rangle|^2\rho_f(E_p)\,\mathrm{sinc}^2(x)\,dx$$

Fermi's Golden Rule approximates this result in the limit that the rapid variation of the sinc function takes place on a scale over which the other factors scarcely change: we can take them out of the integral (evaluated at the peak, $\Delta E = 0$ or $E_p = E_i + \hbar\omega$), and we can formally extend the range to $\pm\infty$.

$$\int_0^\infty |a_p^{(1)}(T)|^2\,dp \approx \frac{|\langle p|\,V\,|i\rangle|^2 2t}{\hbar}\rho_f(E(p))\int_{-\infty}^\infty \mathrm{sinc}^2(x)\,dx$$

The integral is π, so finally, expressing the result as a rate of excitation:

$$\boxed{\text{Fermi's Golden Rule:} \qquad \text{Rate} = \frac{2\pi}{\hbar} |\langle p| V |i\rangle|^2 \rho(E).}$$

Simplest Possible Example of Fermi's Golden Rule

The simplest system with a bound state as well as a continuum is a negative delta-function potential $V(x) = -W\delta(x)$ — a sort of limiting narrow deep square well.
This has a single bound state:

$$|i\rangle \quad \text{with} \quad E_i = -\frac{mW^2}{2\hbar^2} \quad \text{and} \quad \langle x|\, i\rangle = \frac{\hbar}{\sqrt{mW}} \exp\left(-mW|x|/\hbar^2\right)$$

and two continuum states for every positive value of E, one even parity and one odd parity:

$$|p, \pm\rangle \quad \text{with} \quad E(p) = \frac{\hbar^2 p^2}{2m} \quad \text{and} \begin{cases} \langle x|\, p, -\rangle = \frac{1}{\sqrt{\pi\hbar}} \sin\left(\frac{px}{\hbar}\right) \\ \langle x|\, p, +\rangle = \frac{1}{\sqrt{\pi\hbar}} \cos\left(\frac{p|x|}{\hbar} + \phi\right) \quad \text{where } \tan\phi = \frac{\pi m W}{p\hbar} \end{cases}$$

We perturb this system with $-Fxe^{-i\omega t}$, so that only the odd-parity states contribute. Thus we use the above results with $|p\rangle$ replaced by $|p, -\rangle$.

Schrodinger Equation:

$$\mathrm{i}\hbar\frac{d}{dt}|\psi\rangle = H_0|\psi\rangle + V(t)|\psi\rangle$$

so in a time δt the increment to the ket is

$$\delta|\psi\rangle = \left[\frac{-\mathrm{i}H_0}{\hbar}|\psi\rangle + \frac{-\mathrm{i}V(t)}{\hbar}|\psi\rangle\right]\delta t.$$

The first term provides the usual time-dependence for energy eigenstates $|E\rangle$, rotating them (clockwise!) in the complex plane with angular frequency $E/\hbar$.

The second term gives the transitions between eigenstates.

We can project the ket increment onto the energy eigenstates (just the second term):

$$\delta|\psi\rangle = \sum_E |E\rangle\langle E|\frac{iV(t)}{\hbar}|\psi\rangle\,\delta t$$

so so to get to a particular final state E_f this must be non-zero: the ket increment must not be orthogonal to $|E\rangle$ (and the more similar they are the bigger the probability of transition).

The initial state is rotating in complex plane at $E_i/\hbar$; the little bit of state $|E_f\rangle$ rotates at $E_f/\hbar$, so the successive increments cancel out unless the time-dependence of $V(t)$ contains a part which rotates at the correct difference frequency $(E_f - E_i)/\hbar$.

This gives the expected distribution of material in Trinity Term by lecture:

1 Review of Time-dep't Perturbation Theory/ Selection Rules

2 Selection Rules / Identical Particles

3 Identical Particles / *Atomic Hamiltonian*

4 Atomic Units: Hydrogen, Helium

5 Helium: Exact Symmetries, Perturbation Theory

6 Helium: Variational Principle

7 Helium: quick look at modern calculations / Questions.

Selection Rules are Conservation Laws

Of all the possible transitions between states of an atom only a quite small subset occur at any significant rate. These possible transitions are determined by Selection Rules.

One way of looking at selection rules is that they represent conservation laws — a transition not obeying the selection rule would violate the conservation law.

The obvious conservation laws are:

Energy: $E_i = E_f \pm \hbar\omega$ (for emission/absorption). This is *Bohr's Frequency Rule,* and we have seen how it comes out of time-dependent perurbation theory. It's not a constraint on what transitions $i \to f$ can occur.

Momentum: This is also conserved in radiative processes, but the emitted or absorbed momentum is taken up by the atom as a whole.
So more exactly, for emission of a photon with wavevector $\mathbf{k} = (\omega/c)\mathbf{n}$:

$$\begin{aligned} \mathcal{E}_i &= \mathcal{E}_f + \hbar\omega \\ \mathbf{p}_i &= \mathbf{p}_f + \hbar\mathbf{k} \end{aligned} \qquad \text{where} \qquad \begin{aligned} \mathcal{E}_i &= E_i + \frac{p_i^2}{2M} \\ \mathcal{E}_f &= E_f + \frac{p_f^2}{2M} \end{aligned}$$

This does not constrain the transitions $i \to f$ either.

Angular Momentum: This turns out to give an important selection rule.

$$\text{A.M of initial state} = \text{ A.M of final state} + \text{A.M. of radiation Field}$$

The *Total* A.M. of the electrons in the atom is usually given the symbol J.
(If the nucleus is included as well it's called F, but strictly speaking the selection rule applies to whatever is the total A.M. of the atom.)

The A.M. of the radiation field can't be less than $1\hbar$, (the spin of the photon), but can be more: spatial structure in the field can carry additional A.M.
Different interaction multipoles (dipole, quadrupole . . .) carry different amounts of A.M.

We shall just consider the lowest multipole (dipole) and the strongest case (electric).
In this case the A.M. is $1\hbar$, and the interaction Hamiltonian is $-\mathbf{E}\cdot\mathbf{D}$, where $\mathbf{D} = -e\sum_i \mathbf{r}_i$ summed over the electrons.

The addition of the angular momentum of the two parts of the system require the Rules for the Addition of Angular Momenta:

Rules for the Addition of Angular Momenta

The possible angular momentum quantum numbers for a system composed of two subsystems with angular momenta quantum numbers of J_1 and J_2 are given by J where:

The maximum value of J is $J_{\text{max}} = J_1 + J_2$;

The minimum value of J is $J_{\text{min}} = |J_1 - J_2|$;

J goes from J_{min} to J_{max} in steps of 1.

The selection rule is simply that there must be a way of couple the two angular momenta of the final state to give the same as the initial state:

So if the final state involves adding J_f and 1, the possible final angular momenta are from $J_f + 1$ to $|J_f - 1|$. Obviously this depends on the value of J_f:

If $J_f \geq 1$ then the range of possibilities is $J_i = J_f + 1,\ J_f,\ J_f - 1$.
If $J_f = \frac{1}{2}$ then we can have $J_i = \frac{3}{2}$ or $\frac{1}{2}$.
If $J_f = 0$ then the only possible J_i is 1.

We can summarize this as $\boxed{\Delta J = 0,\ \pm 1 \quad 0 \not\rightarrow 0.}$

This expresses the exchange of one unit of A.M. between the atom and the radiation field.

Selection Rules are Symmetries

Another way of looking at selection rules is that they follow from symmetries. For example the atomic Hamiltonian always commutes with the Parity operator P:

$$[P, H] = 0$$

and hence we can choose atomic eigenstates to be eigenstates of P. Thus all atomic states have a parity quantum number of $p = \pm 1$.

However the electric dipole interaction Hamiltonian *anti-commutes* with P:

$$P\,\mathbf{E}\cdot\mathbf{D} = -\mathbf{E}\cdot\mathbf{D}\,P \qquad \text{or} \qquad \{P, H_{\text{int}}\} = 0.$$

(This is because P acts on $\mathbf{D}$ and not $\mathbf{E}$. If we enlarge the scope of P to act on the field variables as well then we recover the expected commutator, not anti-commutator.)

Take a matrix element of the anti-commutator (repeat of Stark effect argument):

$$\langle f|\, P\mathbf{D} + \mathbf{D}P\, |i\rangle = (p_f + p_i)\,\langle f|\,\mathbf{D}\,|i\rangle = 0$$

So either $p_i = -p_f$, the states have opposite parity, or the matrix element is zero.

So the Selection Rule is $\boxed{\text{Parity Changes}}$ which is usually summarised as $\boxed{\text{YES}}$

(Conservation law view: Parity is conserved, but both and atom and field change.)

Selection Rules follow from Commutators

We have already seen this for P; it is also true for J. The relevant commutator is

$$[J_i, D_j] = \mathrm{i}\epsilon_{ijk}\hbar D_k \qquad \text{or} \quad [J_x, D_y] = \mathrm{i}\hbar D_z \quad \text{and cyclically.}$$

This is true simply because **D** is a vector operating on the atomic variables, and **J** is the total atomic angular momentum. This is a very powerful argument because of its generality: $S(\alpha) = (1 - \mathrm{i}\alpha J_z/\hbar)$ rotates the atomic state by the infinitesimal angle α around the z-axis. When we do this the matrix elements of a vector operator must behave as vectors:

$$\langle f| S^\dagger(\alpha) D_x S(\alpha) |i\rangle = \langle f| D_x |i\rangle - \alpha \langle f| D_y |i\rangle \,.$$

If we keep terms to first order on the left:

$$\langle f| D_x |i\rangle + \frac{\mathrm{i}\alpha}{\hbar} \langle f| J_z D_x - D_x J_z |i\rangle = \langle f| D_x |i\rangle - \alpha \langle f| D_y |i\rangle \,,$$

giving the zx version of the commutator.

We now use the fact that the free-atom states will be eigenstates of angular momentum: replace $|i\rangle$ with $|J_iM_i\rangle$ and similarly for the final state. Then the three commutators with J_z give the selection rule on M:

$$[J_z, D_z] = 0 : \quad \langle J_f M_f| \, J_z D_z - D_z J_z \, |J_i M_i\rangle = (M_f - M_i)\hbar \, \langle J_f M_f| \, D_z \, |J_i M_i\rangle = 0$$

The other two are $[J_z, D_x] = i\hbar D_y$ and $[J_z, D_y] = -\mathrm{i}\hbar D_x$ or $[J_z, D_x \pm \mathrm{i}D_y] = \pm\hbar(D_x \pm \mathrm{i}D_y)$. Again we take a general matrix element:

$$\langle J_f M_f| \, J_z D_\pm - D_\pm J_z \, |J_i M_i\rangle = (M_f - M_i)\hbar \, \langle J_f M_f| \, D_\pm \, |J_i M_i\rangle = \pm\hbar \, \langle J_f M_f| \, D_\pm \, |J_i M_i\rangle$$

$$(M_f - M_i \mp 1)\hbar \, \langle J_f M_f| \, D_\pm \, |J_i M_i\rangle = 0.$$

We can summarize this as $\boxed{\Delta M_J = 0, \, \pm 1.}$

We can also derive the ΔJ rule from a commutator.

We can use the commutator method to generate more selection rules:

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \quad \text{where} \quad \mathbf{L} = \sum_{\text{electrons}} \boldsymbol{l}_i \quad \text{and} \quad \mathbf{S} = \sum_{\text{electrons}} \mathbf{s}_i$$

(Note the emerging typographical convention: we use upper case letters for whole atom quantities and lower case for single electron quantities.)

Now the transition operator $\mathbf{D}$ does not involve S at all:

$$[S_i, D_j] = 0 \qquad \text{and hence} \quad [L_i, D_j] = [J_i - S_i, D_j] = \mathrm{i}\hbar\epsilon_{ijk} D_k.$$

If the atomic state is an eigenstate of L^2 and S^2:

$$\langle L_f S_f J_f M_f | \, S^2\mathbf{D} - \mathbf{D}S^2 \, | L_i S_i J_i M_i \rangle = \Big(S_f(S_f+1) - S_i(S_i+1) \Big) \hbar^2 \langle L_f S_f J_f M_f | \, \mathbf{D} \, | L_i S_i J_i M_i \rangle = 0$$

which means the rate is zero unless $\boxed{\Delta S = 0.}$

The second commutator is the same as the J commutator so the selection rule is identical:

$$\boxed{\Delta L = 0, \pm 1 \quad 0 \not\to 0.}$$

In multi-electron atoms these rules are only approximate because whereas the state of the free atom *is* an eigenstate of J^2, it is only approximately an eigenstate of L^2 and S^2.

Suppose we have a state of two non-interacting particles in the same gravitational potential (I'm only using gravity because if they are non-interacting they had better be electrically neutral!):

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + m\phi(\mathbf{r}_1) + m\phi(\mathbf{r}_2)$$

This acts on a ket $|\psi\rangle$, and there is a complete set of basis kets $|\mathbf{r}_1, \mathbf{r}_2\rangle = |\mathbf{r}_1\rangle |\mathbf{r}_2\rangle$ representing a state in which particle i is at $\mathbf{r}_i$.

What sort of eigenstates can we expect to find?

There is an obvious symmetry — both particles are identical so they appear in the Hamiltonian in identical ways. (If they didn't we could use the difference to distingush between them.) To make it more formal we introduce an exchange operator P_{12} which swaps particle labels:

$$P_{12}\frac{p_1^2}{2m} = \frac{p_2^2}{2m}\text{etc} \qquad \text{and hence} \quad [P_{12}, H] = 0.$$

Thus it appears that eigenstates of H can be chosen to be eigenstates of P_{12}.

$P_{12}^2 = 1$ and so the eigenstates are either symmetric $P_{12}|\psi\rangle = |\psi\rangle$ or antisymmetric $P_{12}|\psi\rangle = -|\psi\rangle$. But the vanishing $[P_{12}, H]$ commutator doesn't just apply to this situation: it will be true for any other interaction we care to introduce. It simply depends on the indistinguishability of the two particles.

Thus neither this Hamiltonian nor any other possible Hamiltonian can distinguish between the two particles so $[P_{12}, H] = 0$ for all situations.

But this means that two particles in a symmetric state will always remain in a symmetric state (compare the argument for the Parity selection above). So at the foundation of the world some of these identical particles were put in symmetric and some into antisymmetric states . . . *this is getting ridiculous!*

It is not so! For any given particle the wavefunction is either always symmetric under P_{12}, or always antisymmetric, depending on the particle. Particles with symmetric wavefunctions obey Bose-Einstein statistics, and are known as *bosons,* and particles with antisymmetric wavefunctions obey Fermi-Dirac statistics and are known as *fermions.*

How do we know which is which? The **Spin-Statistics Theorem** states:

Particles with integer spin are bosons, and particles with half-integer spin are fermions.

Thus electrons, protons, neutrons, ^{3}He nuclei are fermions, deuterium nuclei, hydrogen atoms and alpha particles are bosons.
That electron wavefunctions are antisymmetric under P_{12} is known as the Pauli principle.
(Nomenclature complex here.)

The atom consists of N electrons (charge $-e$, mass m, labelled 1 to N) and a nucleus (charge Ze, mass M, labelled 0). The mass of the atom is $\mathcal{M} = M + Nm$.

The Hamiltonian is the energy function of the atom. The biggest terms are obvious:

$$H_0 = \sum_i \frac{P_i^2}{2m} \qquad \text{Kinetic energy of the electrons}$$

$$- \sum_i \frac{Ze^2}{4\pi\epsilon_0 R_i} \qquad \text{Electrostatic electron-nucleus potential energy}$$

$$+ \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 R_{ij}} \qquad \text{Electrostatic electron-electron potential energy}$$

What does this leave out? There are at least five categories of omitted terms:

(1) Relativistic correction to non-relativistic kinetic energy

(2) Kinetic energy of the nucleus

(3) Finite size of the nuclear charge distribution

(4) Other corrections to the electron-nucleus interaction

(5) Corrections to the electron-electron interaction

1. Relativistic Correction to the Kinetic Energy

This takes the same form as in Hydrogen for each electron:

$$\boxed{H_1 = \sum_i -\frac{P_i^4}{8m^3c^2}}$$

2. Kinetic Energy of the Nucleus

Our starting point H_0 treats the nucleus as fixed at the origin — and so, in effect, infinitely massive. The configuration of the system is defined by the N positions $\mathbf{R}_1 \ldots \mathbf{R}_N$.

We can easily give the nucleus a variable position $\mathbf{R}_0$ (with corresponding change $R_i \to R_{i0}$ in the electron-nuclear distance) and then include a term

$$H_2 = \frac{P_0^2}{2M}.$$

However it's not so simple ...

By giving the system three more degrees of freedom, it is no longer fixed to the origin - the whole atom can now move! We need to remove this free-particle degree of freedom to discover what the energy of the system is in the centre-of-mass frame.

We do this with a co-ordinate change:

$$\mathbf{r}_0 = \frac{M\mathbf{R}_0 + \sum_j m\mathbf{R}_j}{\mathcal{M}} \qquad \text{Centre of Mass}$$

$$\mathbf{r}_i = \mathbf{R}_i - \mathbf{R}_0 \qquad \text{Electron } i \text{ relative to Nucleus}$$

We need to find out what the new conjugate momenta are — *i.e.* we have to find out what the operators $\boldsymbol{\mathcal{P}} = -i\hbar\nabla_0$ and $\mathbf{p}_i = -i\hbar\nabla_i$ represent.
In fact the algebra is shorter if we proceed backwards(!):

$$P_{X0} = -i\hbar\frac{\partial}{\partial X_0} = -i\hbar\frac{\partial x_0}{\partial X_0}\frac{\partial}{\partial x_0} - i\hbar\sum_i \frac{\partial x_i}{\partial X_0}\frac{\partial}{\partial x_i} \qquad P_{Xi} = -i\hbar\frac{\partial x_0}{\partial X_i}\frac{\partial}{\partial x_0} - i\hbar\sum_i \frac{\partial x_i}{\partial X_i}\frac{\partial}{\partial x_i}$$

Reading off the partial differentials

$$\mathbf{P}_0 = \frac{M}{\mathcal{M}}\boldsymbol{\mathcal{P}} - \sum_i \mathbf{p}_i \qquad \mathbf{P}_i = \frac{m}{\mathcal{M}}\boldsymbol{\mathcal{P}} + \mathbf{p}_i \quad \text{and hence} \quad \boldsymbol{\mathcal{P}} = \mathbf{P}_0 + \sum_i \mathbf{P}_i$$

Thus $\boldsymbol{\mathcal{P}}$ (the momentum conjugate to $\mathbf{r}_0$) represents the total momentum of the atom in the original reference frame, and hence $\boldsymbol{\mathcal{P}}/\mathcal{M}$ represents the velocity of the centre of mass $\boldsymbol{\mathcal{V}}$. Then $\mathbf{p}_i = \mathbf{P}_i - m\boldsymbol{\mathcal{V}} = m(\mathbf{V} - \boldsymbol{\mathcal{V}})$ is the momentum in the centre-of-mass frame.

Thus although our co-ordinate is $\mathbf{r}_i = \mathbf{R}_i - \mathbf{R}_0$, the position relative to the *nucleus,* the conjugate momentum $\mathbf{p}_i$ represents the mass × velocity relative to *centre of mass.*

The momentum of the nucleus in the centre-of-mass frame is $\mathbf{P}_0 - M\boldsymbol{\mathcal{V}}$, which we define to be $\mathbf{p}_0 = \mathbf{P}_0 - M\boldsymbol{\mathcal{V}} = -\sum_i \mathbf{p}_i$.

To complete the calculation we find the total kinetic energy in terms of the new momenta:

$$\sum_i \frac{P_i^2}{2m} + \frac{P_0^2}{2M} = \sum_i \frac{(\frac{m}{\mathcal{M}}\boldsymbol{\mathcal{P}} + \mathbf{p}_i)^2}{2m} + \frac{(\frac{M}{\mathcal{M}}\boldsymbol{\mathcal{P}} + \mathbf{p}_0)^2}{2M} = \frac{\boldsymbol{\mathcal{P}}^2}{2\mathcal{M}} + \sum_i \frac{\mathbf{p}_i^2}{2m} + \frac{\mathbf{p}_0^2}{2M}$$

which nicely splits into the free-particle term, the electronic term (but relative to centre of mass instead of fixed origin) and a new term representing the kinetic energy of the nucleus:

$$\boxed{H_2 = \frac{\left(-\sum_i \mathbf{p}_i\right)^2}{2M}}$$

Standard Atomic Units

If we adopt units in which Planck's constant $\hbar$, the elementary charge e, the mass of the electron m_e and $4\pi\epsilon_0$ are all 1 then we eliminate a lot of scaling factors in Hamiltonians, and this is the standard set of atomic units. We can use these quantities to define units of mass, length, time and current, and so they form a complete set of units:

Constant	Dimensions	
m_e	$[M]$	
$\hbar$	$[ML^2T^{-1}]$	
$e^2/4\pi\epsilon_0$	$[ML^3T^{-2}]$	
Quantity	**Unit**	**Name**
Length $[L]$	$\dfrac{\hbar^2}{m_e e^2/4\pi\epsilon_0}$	Bohr radius a_0
Time $[T]$	$\dfrac{\hbar^3}{m_e(e^2/4\pi\epsilon_0)^2}$	
Velocity $[LT^{-1}]$	$\dfrac{e^2}{4\pi\epsilon_0\hbar}$	
Energy $[ML^2T^{-2}]$	$\dfrac{m_e(e^2/4\pi\epsilon_0)^2}{\hbar^2}$	Hartree $\mathcal{H}_0$

Scaling the Hydrogen Hamiltonian

The Hamiltonian for the internal motion in any hydrogen-like atom (neglecting relativistic terms) is

$$H = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{\hbar^2}{2M}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

where the nucleus has charge Ze and mass M, and $\mu = m_e M/(m_e + M)$ is the reduced mass. There are quite a lot of different systems described by this Hamiltonian, with different values of Z and μ, or $\zeta = \mu/m_e$:

System	Z	ζ		
Hydrogen	1	$\frac{m_p}{m_p+m_e}$	$\approx$	1
Deuterium	1	$\frac{m_d}{m_d+m_e}$	$\approx$	1
^{4}He$^+$	2	$\frac{m_\alpha}{m_\alpha+m_e}$	$\approx$	1
Hydrogen-like Z	Z	$\frac{m_Z}{m_Z+m_e}$	$\approx$	1
Muonium	1	$\frac{m_\mu}{m_\mu+m_e}$	$\approx$	1
Positronium	1	$\frac{1}{2}$		
Muonic Z	Z	$\frac{m_Z}{m_Z+m_\mu}\frac{m_\mu}{m_e}$	$\approx$	207

Scaled Atomic Units

However the constants appearing in this Hamiltonion are not the ones we used to define the units: we have μ instead of m_e and Ze^2 instead of e^2. With these replacements we get:

$$\text{Length:} \qquad a(Z,\zeta) = \frac{\hbar^2}{\mu Z e^2/4\pi\epsilon_0} = \frac{a_0}{Z\zeta}$$

$$\text{Energy:} \qquad \mathcal{H}(Z,\zeta) = \frac{\mu Z^2 e^4}{(4\pi\epsilon_0)^2\hbar^2} = \zeta Z^2 \mathcal{H}_0.$$

We switch to these units by defining $\mathbf{r} = a(Z,\zeta)\mathsf{r}$ $\quad E = \mathcal{H}(Z,\zeta)\mathsf{E}$ and this strips out all the constants from the Schrödinger equation:

$$-\frac{1}{2}\nabla^2\psi - \frac{1}{|\mathsf{r}|}\psi = \mathsf{E}\psi.$$

This has eigenvalues $\mathsf{E}_{nlm} = -\dfrac{1}{2n^2}$ and the wavefunctions are, for example, $\psi_{100} = \dfrac{e^{-|\mathsf{r}|}}{\sqrt{\pi}}$.

This is a remarkable result: all these distinct systems have the *same* eigenvalues and wavefunctions — apart from the scaling factors. All the system properties for hydrogen can be scaled appropriately and apply to positronium or He$^+$.

However if we add in the relativistic correction terms in H this is no longer exactly true: they have system-dependent scaling factors even after the switch to these variables. (Also, in the case of Ps, we may have to reconsider terms neglected because of their ‘nuclear’ mass-dependence)

Consider the relativistic correction to the electron kinetic energy:

$$H_1 = -\frac{p^4}{8m^3c^2} = -\left(\frac{\hbar^4}{8m^3c^2a^4}\right)\mathsf{p}^4 = (Z^2\zeta^3)\mathcal{H}(Z,\zeta)\left(-\frac{\alpha^2}{8}\mathsf{p}^4\right).$$

Thus at this level the system-dependent constants remain: we see that in He$^+$ this term is *relatively* $Z^2 = 4$ times bigger than in Hydrogen (neglecting the small change in ζ), and absolutely $Z^4 = 16$ times bigger.

In positronium it is relatively smaller by $\zeta^3 = 1/8$ and absolutely smaller by $1/16$, and we have to include the corresponding term for the positron which in an ordinary nuclear atom is much smaller because of the M^3 dependence.

Application to Helium-like systems

An atom with two electrons has the Hamiltonian (neglecting all relativistic and magnetic terms)

$$H=\sum_{i=1,2}\left(\frac{\mathbf{p}_i^2}{2m_e}-\frac{Ze^2}{4\pi\epsilon_0 r_i}\right)+\frac{e^2}{4\pi\epsilon_0 r_{12}}+\frac{(-\mathbf{p}_1-\mathbf{p}_2)^2}{2M}$$

If we expand out the nuclear kinetic energy:

$$H=\sum_{i=1,2}\left(\frac{\mathbf{p}_i^2}{2\mu}-\frac{Ze^2}{4\pi\epsilon_0 r_i}\right)+\frac{e^2}{4\pi\epsilon_0 r_{12}}+\frac{\mathbf{p}_1\cdot\mathbf{p}_2}{M}$$

It *looks* as though the same Z and μ-scaled atomic units will simplify H:

$$H=\mathcal{H}(Z,\zeta)\left[\sum_{i=1,2}\left(\frac{\mathsf{p}_i^2}{2}-\frac{1}{|\mathsf{r}_i|}\right)+\frac{1}{Z}\frac{1}{|\mathsf{r}_{12}|}+\frac{\mu}{M}\mathsf{p}_1\cdot\mathsf{p}_2\right].$$

But in this case we *can't* eliminate the system-dependent factors from the scaled Hamiltonion — the fact that we can for Hydrogen is (yet another) special result. Every He-like system is a fundamenatally different problem. We shall therefore make the usual choice of mass-scaled but not Z-scaled units:

Exact Analysis: Symmetries

$$\boxed{H = \mathcal{H}(1,\zeta)\left[\sum_{i=1,2}\left(\frac{\mathbf{p}_i^2}{2} - \frac{Z}{|\mathbf{r}_i|}\right) + \frac{1}{|\mathbf{r}_{12}|} + \frac{\mu}{M}\mathbf{p}_1\cdot\mathbf{p}_2\right].}$$

We start with some analysis on H to find out what properties its eigenkets will have.

A complete set of kets is provided by position and spin eigenstates $|\mathbf{r}_1, \mathbf{r}_2, \sigma_1, \sigma_2\rangle$ in which particle i is at $\mathbf{r}_i$, and has z-component of spin σ_i which can be either $\pm\frac{1}{2}$.
Thus $\langle \mathbf{a}, \mathbf{b}, \alpha, \beta | \psi\rangle$ where $\mathbf{a}$, $\mathbf{b}$ are position vectors, and α, β are ± 1, is the amplitude for the configuration with electron 1 at $\mathbf{a}$ with spin α and electron 2 at $\mathbf{b}$ with spin β.

Obviously $[P_{12}, H] = 0$ and we require fermionic antisymmetry:

$$\langle \mathbf{a}, \mathbf{b}, \alpha, \beta | P_{12} | \psi\rangle = \langle \mathbf{b}, \mathbf{a}, \beta, \alpha | \psi\rangle = -\langle \mathbf{a}, \mathbf{b}, \alpha, \beta | \psi\rangle$$

We define operators R_{12} and S_{12} which exchange position and spin labels ($P_{12} = R_{12}S_{12}$):

$$\langle \mathbf{a}, \mathbf{b}, \alpha, \beta | R_{12} | \psi\rangle = \langle \mathbf{b}, \mathbf{a}, \alpha, \beta | \psi\rangle \qquad \langle \mathbf{a}, \mathbf{b}, \alpha, \beta | S_{12} | \psi\rangle = \langle \mathbf{a}, \mathbf{b}, \beta, \alpha | \psi\rangle .$$

H contains no spin operators, so that $[R_{12}, H] = [S_{12}, H] = 0$. Hence the eigenkets can be eigenkets of both R_{12} and S_{12}.

We can safely assume that $[\mathbf{J}, H] = 0$, where $\mathbf{J} = \mathbf{L} + \mathbf{S}$ is the total angular momentum.

But since H contains no spin operators $[\mathbf{S}, H] = 0$, and also $[\mathbf{L}, H] = 0$.

However $[\boldsymbol{l}_1, H]$ is non-zero because of the electron-electron interaction term:

$$[\boldsymbol{l}_1, H] = \left[\mathsf{r}_1 \wedge \mathsf{p}_1, \frac{1}{|\mathsf{r}_{12}|} + \frac{\mu}{M}\mathsf{p}_1 \cdot \mathsf{p}_2\right] \quad \text{and} \quad \left[\mathsf{r}_1 \wedge \mathsf{p}_1, \frac{1}{|\mathsf{r}_{12}}|\right] = -\mathrm{i}\frac{\mathsf{r}_1 \wedge \mathsf{r}_2}{|\mathsf{r}_{12}|^3} \neq 0$$

So the eigenkets can be eigenkets of any component of $\mathbf{L}$ and $\mathbf{S}$, but not of the single-electron angular momenta.

Finally H commutes with parity P (as do all atomic Hamiltonians) $[H, P] = 0$.

How many of these are simultaneously possible — that is, how many of these operators commute with each other as well as with H?
All except for the fact that the different components of angular momenta do not commute ($[L_x, L_y] = \mathrm{i}L_z$ etc.) We therefore choose to make the states eigenstates of L^2 and L_z etc.

We then find that $[J^2, L_z] \neq 0$ and $[J^2, S_z] \neq 0$.

Summary: The eigenkets of the approximate Helium H can be chosen to be eigenstates of P_{12} (with eigenvalue -1), R_{12}, S_{12}, P, L^2, S^2, and *either* L_z, S_z or J^2, J_z.

Symmetric and Antisymmetric Spin States

We can easily find the required eigenstates of S_{12} by considering just the spin part of our basis kets $|\sigma_1, \sigma_2\rangle$:

$$S_{12}\,|+,+\rangle = |+,+\rangle \qquad S_{12}\,|+,-\rangle = |-,+\rangle$$
$$S_{12}\,|-,-\rangle = |-,-\rangle \qquad S_{12}\,|-,+\rangle = |+,-\rangle$$

Thus two of the four states are symmetric, and the other two have no definite symmetry. But we can easily find normalised symmetric or anti-symmetric combinations:

$$S_{12}\frac{1}{\sqrt{2}}\left[|+,-\rangle + |-,+\rangle\right] = \frac{1}{\sqrt{2}}\left[|-,+\rangle + |+,-\rangle\right] = +\frac{1}{\sqrt{2}}\left[|+,-\rangle + |-,+\rangle\right]$$
$$S_{12}\frac{1}{\sqrt{2}}\left[|+,-\rangle - |-,+\rangle\right] = \frac{1}{\sqrt{2}}\left[|-,+\rangle - |+,-\rangle\right] = -\frac{1}{\sqrt{2}}\left[|+,-\rangle - |-,+\rangle\right]$$

So there are *three* symmetric spin states (S_{12} eigenvalue $+1$) and *one* antisymmetric spin state (S_{12} eigenvalue -1). These must be combined with spatial states of the *opposite* symmetry so that the overall P_{12} symmetry is antisymmetric (P_{12} eigenvalue -1).

Spin properties of the symmetrised states

Having decided on symmetric and antisymmetric spin states we now expect to find eigenstates of total spin S^2 and S_z. The S_z part is easy:

$$\mathsf{S}_z = \mathsf{s}_{1z} + \mathsf{s}_{2z} \qquad \text{and we know} \qquad \mathsf{s}_{1z} \left|+\right\rangle = \frac{1}{2} \left|+\right\rangle .$$

Thus we can easily deduce

$$\mathsf{S}_z \left|+,+\right\rangle = \left(\frac{1}{2} + \frac{1}{2}\right) \left|+,+\right\rangle = (+1) \left|+,+\right\rangle \qquad \mathsf{S}_z \left|+,-\right\rangle = 0$$

$$\mathsf{S}_z \left|-,-\right\rangle = \left(\frac{-1}{2} + \frac{-1}{2}\right) \left|-,-\right\rangle = (-1) \left|-,-\right\rangle \qquad \mathsf{S}_z \left|-,+\right\rangle = 0$$

Thus S_z eigenvalues: the three symmetric states have $+1$, 0, -1, and the antisymmetric state has 0.

The S^2 part needs a bit more work: $\mathsf{S}^2 = (\mathsf{s}_1 + \mathsf{s}_2)^2 = \mathsf{s}_1^2 + \mathsf{s}_2^2 + 2\mathsf{s}_1 \cdot \mathsf{s}_2$. We can expand the final term:

$$2\mathsf{s}_1 \cdot \mathsf{s}_2 = 2\mathsf{s}_{1x}\mathsf{s}_{2x} + 2\mathsf{s}_{1y}\mathsf{s}_{2y} + 2\mathsf{s}_{1z}\mathsf{s}_{2z} = \mathsf{s}_{1+}\mathsf{s}_{2-} + \mathsf{s}_{1-}\mathsf{s}_{2+} + 2\mathsf{s}_{1z}\mathsf{s}_{2z}.$$

We know the effect of the individual electron s^2 and s_+ or s_- operators:

$$\mathsf{s}^2\,|\pm\rangle = s(s+1)\,|\pm\rangle = \frac{3}{4}\,|\pm\rangle \qquad \mathsf{s}_+\,|+\rangle = 0 \quad \mathsf{s}_+\,|-\rangle = |+\rangle\,.$$

Hence

$$\mathsf{S}^2\,|+,+\rangle = \left(\frac{3}{4} + \frac{3}{4} + 0 + 0 + 2\,\frac{1}{2}\,\frac{1}{2}\right)|+,+\rangle = 2\,|+,+\rangle$$

and similarly for $|-,-\rangle$, while for the other two we note that $\mathsf{s}_{1+}\mathsf{s}_{2-}\,|-,+\rangle = |+,-\rangle$ so that

$$\mathsf{S}^2\Big[|+,-\rangle \pm |-,+\rangle\Big] = \left(\frac{3}{4} + \frac{3}{4} \pm 1 + 2\,\frac{1}{2}\,\frac{-1}{2}\right)\Big[|+,-\rangle \pm |-,+\rangle\Big].$$

Thus all four states are eigenstates of S^2, with eigenvalues of 2 or 0. What did we expect?

We are adding two angular momenta of $\frac{1}{2}$ so we expect the maximum S quantum number to be 1 and the minimum to be 0. The eigenvalue is $S(S+1)$ which is thus 2 or 0 . . . perfect!

Thus making the spin states symmetric and antisymmetric under S_{12} also made coupled the spins to 0 or 1. We label these states with S,M_S for total spin and z-component:

$$|1,1\rangle = |+,+\rangle \qquad |1,0\rangle = \frac{1}{\sqrt{2}}\left[|+,-\rangle + |+,-\rangle\right]$$

$$|1,-1\rangle = |-,-\rangle \qquad |0,0\rangle = \frac{1}{\sqrt{2}}\left[|+,-\rangle - |+,-\rangle\right].$$

Summary of exact properties of eigenstates

The approximate Hamiltonian containing just non-relativistic kinetic energies and electrostatic interactions has eigenstates denoted by ${}^{2S+1}L$ with the following properties:

${}^3S$, ${}^3P$, ${}^3D\ldots$ using the usual letter code, but now in capitals: $0 \equiv S$, $1 \equiv P$, $2 \equiv D$ etc.

- S_{12} eigenvalue $+1$ with R_{12} eigenvalue -1 ;
- P_{12} eigenvalue -1 (only)
- S^2 eigenvalue $S(S+1) = 2$ ($S = 1$, 'triplets') and S_z eigenvalue $M_S = 0, \pm 1$;
- L^2 eigenvalue $L(L+1)$ with $L = 0, 1, 2\ldots$
- an eigenstate of parity;
- NOT an eigenstate of $\ell_1^2 + \ell_2^2$;

${}^1S$, ${}^1P$, ${}^1D\ldots$

- S_{12} eigenvalue -1 with R_{12} eigenvalue $+1$;
- P_{12} eigenvalue -1 (only)
- S^2 eigenvalue $S(S+1) = 0$ ($S = 0$, 'singlets') and S_z eigenvalue $M_S = 0$;
- L^2 eigenvalue $L(L+1)$ with $L = 0, 1, 2\ldots$
- an eigenstate of parity;
- NOT an eigenstate of $\ell_1^2 + \ell_2^2$;

Perturbation Theory

However these exact properties do not enable us to find the eigenkets or their energies.
The only approach we have to fall back on is Perturbation Theory .
We drop the small nuclear motion terms, and revert to standard atomic units to leave

$$H = \mathcal{H}_0 \left[\sum_{i=1,2} \left(\frac{\mathbf{p}_i^2}{2} - \frac{Z^2}{|\mathbf{r}_i|} \right) + \frac{1}{|\mathbf{r}_{12}|} \right].$$

The term that makes it hard is the $1/\mathbf{r}_{12}$ term — without that it is just two uncoupled hydrogen Hamiltonians. But the coefficient of 1 is not exactly small in comparison with Z, especially in Helium. But this approach might just give some insight in helium-like ions of higher Z.

So we treat the final term using Pertubation Theory.
The unperturbed eigenkets are just products of hydrogenic states with any spin state:

$$|n_1, \ell_1, m_1; n_2, \ell_2, m_2; S, M_S\rangle = |n_1, \ell_1, m_1\rangle \, |n_2, \ell_2, m_2\rangle \, |S, M_S\rangle \, .$$

However these don't have all the symmetries we want (as well as some quantum numbers — n and ℓ — we said we didn't want). But the ground state ($n_1 = n_2 = 1$, $\ell_1 = \ell_2 = 0 \equiv s$) is OK:

$$\left|1s^2\ {}^1S\right\rangle = |1s\rangle\,|1s\rangle\,|0,0\rangle$$

where the spatial state is symmetric so the spin state is antisymmetric, and there is no angular momentum either orbital or spin, and even parity. The zeroth-order energy is two hydrogenic energies:

$$E^{(0)}_{1s^2} = -\frac{Z^2}{2} - \frac{Z^2}{2} = -Z^2 \qquad \text{in units of } \mathcal{H}_0.$$

The general state above has zeroth-order energy

$$E^{(0)}_{n_1 n_2} = -\frac{Z^2}{2n_1^2} - \frac{Z^2}{2n_2^2} \qquad \text{in units of } \mathcal{H}_0.$$

Taking $n_2 \to \infty$ gives a prediction for the 1st ionization energy of $Z^2\mathcal{H}_0/2$, or 54.4 eV for helium — a rotten prediction! But it makes one useful prediction: the state with *both* electrons in $n = 2$ has 1/4 of the binding energy of the ground state, whereas the first ionisation is predicted to be a half: *any doubly excited states are above the first ionisation level.*

So we consider only singly excited states $1sn\ell$:

$$
\begin{aligned}
\text{Ground State:} \quad & \left|1s^{2}\,{}^{1}S\right\rangle = |1s\rangle\,|1s\rangle\,|0,0\rangle \\
\text{Excited Singlet State:} \quad & \left|1sn\ell\,{}^{1}L\right\rangle = \frac{1}{\sqrt{2}}\Big[|1s\rangle\,|n\ell\rangle + |n\ell\rangle\,|1s\rangle\Big]|0,0\rangle \\
\text{Excited Triplet State:} \quad & \left|1sn\ell\,{}^{3}L\right\rangle = \frac{1}{\sqrt{2}}\Big[|1s\rangle\,|n\ell\rangle - |n\ell\rangle\,|1s\rangle\Big]|1,M_S\rangle
\end{aligned}
$$

These states have all the right eigenvalue properties: spin and space exchange symmetry, parity, eigenstates of S^2, L^2, S_z and L_z. (No coupling required in orbital angular momentum because one of the ℓ is zero!) The only problem is that it is also an eigenstate of $\ell_1^2 + \ell_2^2$.

The zeroth-order energies of these states are

$$
E^{(0)}_{1sn\ell} = -\frac{Z^2}{2} - \frac{Z^2}{2n^2} \qquad \text{in units of } \mathcal{H}_0.
$$

Now we have constructed the correct zeroth-order eigenkets and energies we can do some perturbation theory.

First-Order Perturbation Theory

We now evaluate the effect of the electron-electron interaction in perturbation theory:

$$\frac{1}{|\mathsf{r}_{12}|} = \frac{1}{\sqrt{\mathsf{r}_1^2 - 2\mathsf{r}_1 \cdot \mathsf{r}_2 + \mathsf{r}_2^2}} = \frac{1}{\mathsf{r}_>} \frac{1}{\sqrt{1 - 2t\cos\theta_{12} + t^2}}$$

where $\mathsf{r}_>$ is the larger of $|\mathsf{r}_1|$, $|\mathsf{r}_2|$, and $t = \mathsf{r}_</\mathsf{r}_>$. But this is just the generating function for Legendre polynomials so

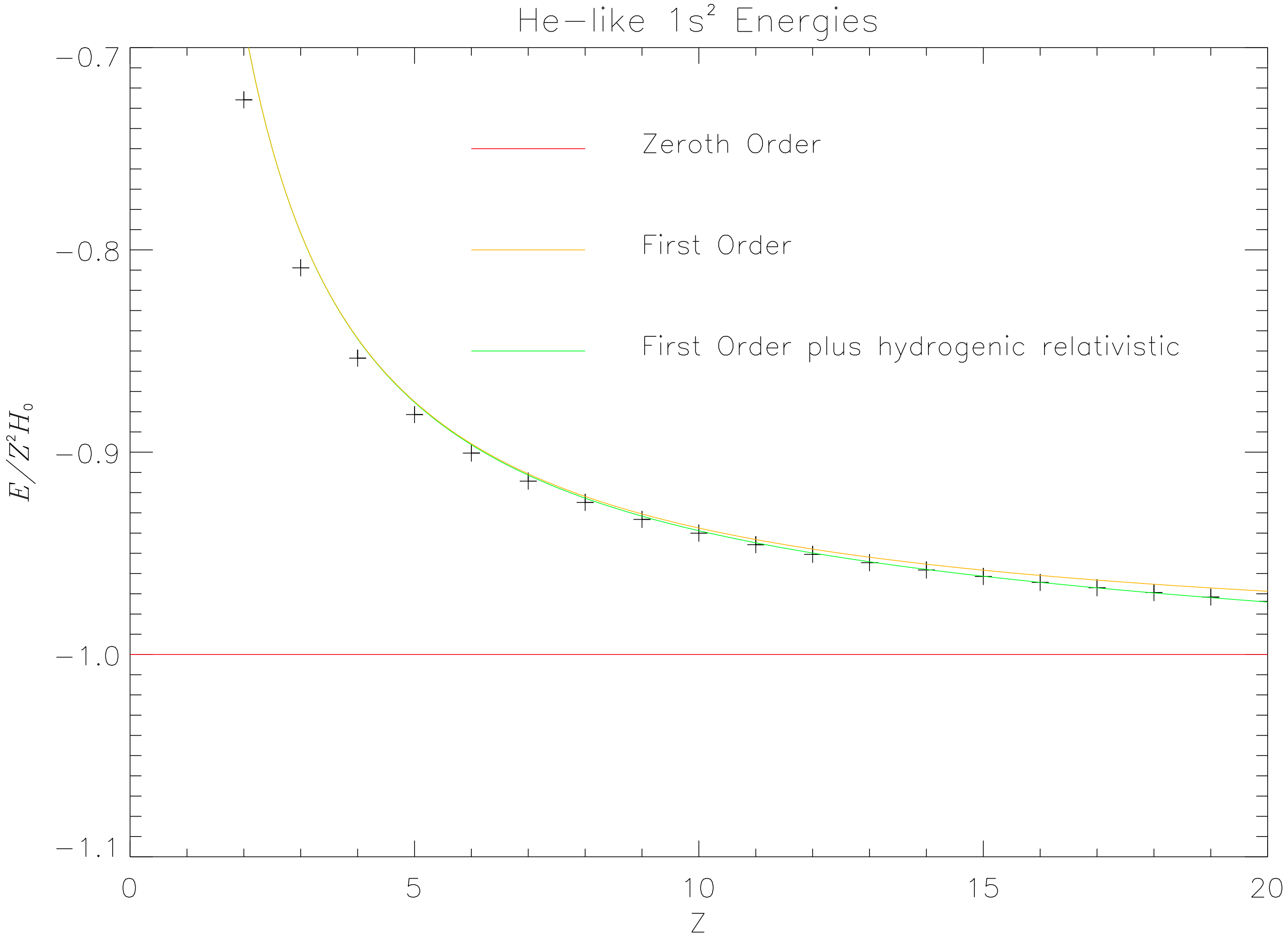
$$\frac{1}{|\mathsf{r}_{12}|} = \sum_{\ell=0}^{\infty} \left(\frac{\mathsf{r}_<^{\ell}}{\mathsf{r}_>^{\ell+1}} \right) P_l(\cos\theta_{12})$$

If we only consider $\ell = 0$, or s, states then we need only consider the first term in the series: the others introduce angular factors that integrate to zero.

For the ground state we have

$$E_{1s^2}^{(1)} = \int \psi_{1s^2}^*(r_1, r_2) \frac{1}{r_>} \psi_{1s^2}(r_1, r_2)\, d^3\mathbf{r}_1\, d^3\mathbf{r}_2\, \mathcal{H}_0 = \frac{Z^6}{\pi^2} \int \frac{1}{\mathsf{r}_>} e^{-2Zr_1} e^{-2Zr_2}\, d^3\mathbf{r}_1\, d^3\mathbf{r}_2\, \mathcal{H}_0.$$

The integral is $5Z/8$ so $E_{1s^2}^{(1)} = (5Z/8)\,\mathcal{H}_0$.


He–like 1s² Energies
Zeroth Order
First Order
First Order plus hydrogenic relativistic
E/Z^2H_0
Z
−0.7
−0.8
−0.9
−1.0
−1.1
0
5
10
15
20

In the excited states we now reap the benefits of putting some effort into the symmetries of the zeroth-order kets: what would otherwise be a degenerate perturbation problem of large order can be treated as non-degenerate because the kets are all eigenkets of operators commuting with H_0 and H_1:

$$E^{(1)}_{1s2s} = \begin{cases} \left\langle 1s2s^3 \right| \frac{1}{r_>} \left| 1s2s^3S \right\rangle \\ \left\langle 1s2s^1 \right| \frac{1}{r_>} \left| 1s2s^1S \right\rangle \end{cases}$$

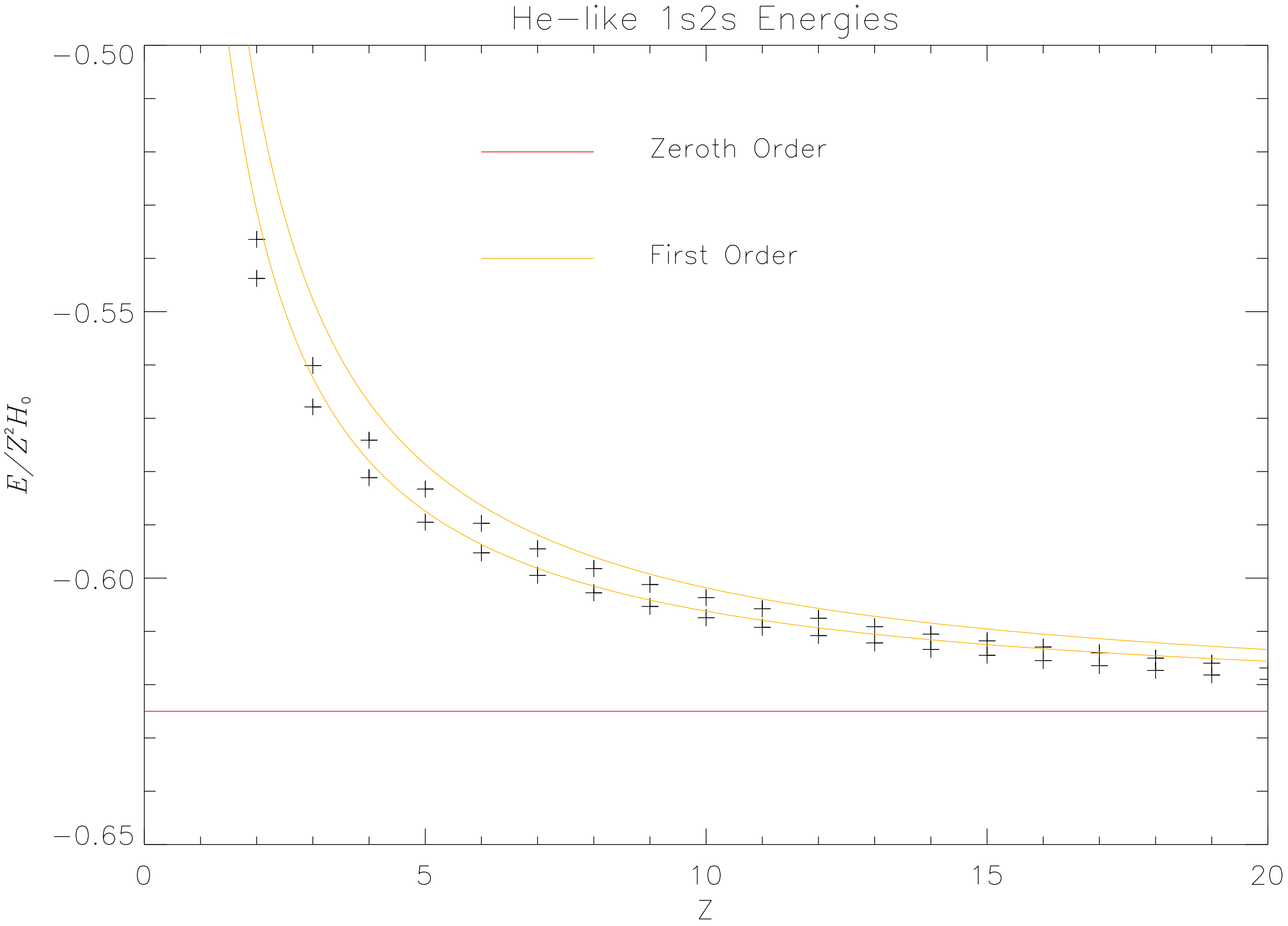
In excited states this method yields two classes of integral:

$$E^{(1)}_{1s2s} = \int |\phi_{1s}(r_1)|^2 \frac{1}{r_>} |\phi_{2s}(r_2)|^2 \, d^3\mathbf{r}_1 \, d^3\mathbf{r}_2 \pm \int [\phi_{1s}(r_1)\phi_{2s}(r_1)] \frac{1}{r_>} [\phi_{1s}(r_2)\phi_{2s}(r_2)] \, d^3\mathbf{r}_1 \, d^3\mathbf{r}_2$$

known as direct and exchange integrals (upper sign for singlet, lower for triplet).

Enthusiasts may care to check that this gives

$$E^{(1)}_{1s2s} = \left(\frac{17}{81} \pm \frac{16}{729} \right) Z\mathcal{H}_0.$$


He−like 1s2s Energies
−0.50
−0.55
−0.60
−0.65
0
5
10
15
20
Z
E/Z²H₀
Zeroth Order
First Order

Variational Theorem

To do better than this we must use a more powerful method. The variational theorem allows us to construct very accurate ground states (or lowest states of given symmetry):

Theorem:

For any ket $|\alpha\rangle$ the expectation value of the Hamiltonian $\langle\alpha| H |\alpha\rangle / \langle\alpha|\alpha\rangle$ is an upper bound for the ground state energy.

Proof:

Expand $|\alpha\rangle$ in energy eigenstates $|\alpha\rangle = \sum_i c_i |E_i\rangle$. Then

$$\frac{\langle\alpha| H |\alpha\rangle}{\langle\alpha|\alpha\rangle} = \frac{\sum_i |c_i|^2 E_i}{\sum_i |c_i|^2} = E_1 + \frac{\sum_i |c_i|^2 (E_i - E_1)}{\sum_i |c_i|^2} \geq E_1.$$

since the last term is positive definite. Equality is obtained iff $|\alpha\rangle = |E_1\rangle$.

All accurate atomic wavefunctions are based in way or another on the variational theorem, either constructing the wavefunction as a sum of analytic functions with variable coefficients, or as a numerical approximation on a grid of points.

For excited states there is an extension, the HUM (Hylleraas-Undheim-MacDonald) Theorem: for a set of trial wavefunctions the n'th eigenvalue of the Hamiltonian matrix gives an upper bound for the n'th excited state.

A very simple variational wavefunction is provided by an effective-Z model: we observe that the electron-electron interaction counteracts the electron nulear interaction by tending to push electrons apart rather than together. So we introduce a different splitting up of $\mathbf{H}$:

$$\mathbf{H} = \left[\sum_{i=1,2} \left(\frac{\mathbf{p}_i^2}{2} - \frac{Z'}{|\mathbf{r}_i|} \right) + \frac{1}{|\mathbf{r}_{12}|} - \sum_{i=1,2} \left(\frac{Z - Z'}{|\mathbf{r}_i|} \right) \right] \mathcal{H}_0.$$

The ground state eigenfunction of the first term is

$$\frac{Z'^3}{\pi} \exp[-Z'(\mathbf{r}_1 + \mathbf{r}_2)],$$

and we use this as our variational wavefunction. The expectation value is given by

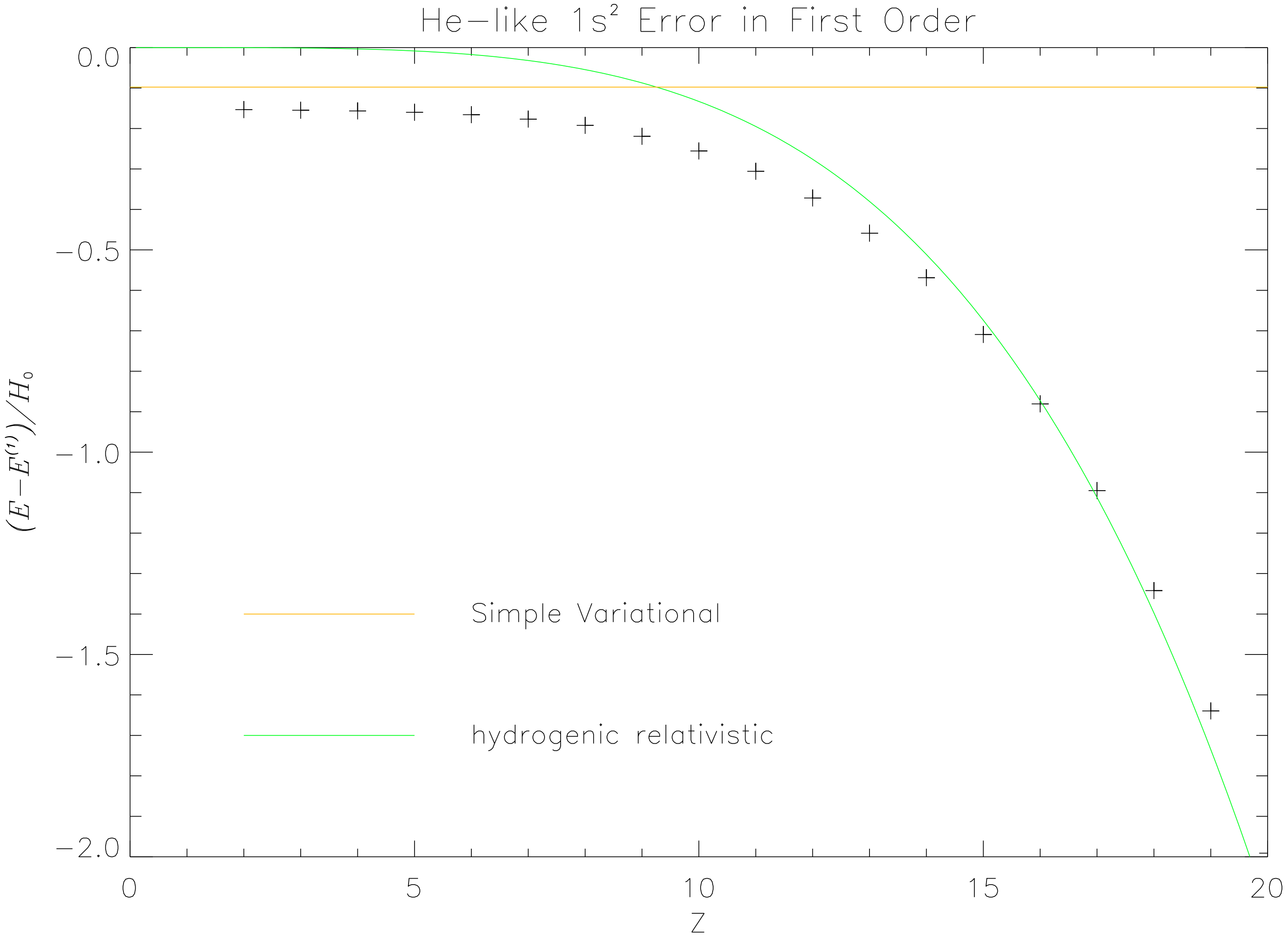
First term: $-Z'^2$

e-e interaction: $\dfrac{5Z'}{8}$

Last term: $-2Z'^2 \dfrac{(Z - Z')}{Z'} = -2Z'(Z - Z')$

giving a total energy of $Z'^2 - (2Z - 5/8)Z'$. This has a minimum:

$$Z'_{\min} = Z - \frac{5}{16} \qquad \mathbf{E}_{\min} = -\left(Z - \frac{5}{16} \right)^2 \mathcal{H}_0.$$


He–like 1s² Error in First Order
$(E-E^{(1)})/H_0$
0.0
−0.5
−1.0
−1.5
−2.0
0
5
10
15
20
Z
Simple Variational
hydrogenic relativistic

Obviously this is somewhat better for Helium but for the higher Z cases it's not really any improvement — because we haven't tackled the fundamental problem of the correlation induced by the electron-electron interaction.

The real problem stems from the fact that the approximate kets we are using are eigenkets of ℓ_i. For the groundstate this implies that the variational wavefunction is of the form $\psi(r_1, r_2)$: the amplitudes

$$\langle r_1\mathbf{n}, r_2\mathbf{n}, \alpha, \beta |\, \psi\rangle \quad \text{and} \quad \langle r_1\mathbf{n}, -r_2\mathbf{n}, \alpha, \beta |\, \psi\rangle$$

are equal. What is needed is an explicit dependence on r_{12} as well.

From a perturbation perspective, the effect of the $1/r_{12}$ perturbation is to mix other configurations, including a small amount of $\left|2p^2\,{}^1S\right\rangle$ into $\left|1s^2\,{}^1S\right\rangle$.

The quantum numbers ℓ_i are thus approximate: giving a rough indication of the property of the state but not exactly true: an important idea in atomic physics.