Contents

0.1 Statevectors and Operators

What are the properties of a vector in a vector space? One of the first properties is that we can add two vectors:

$$|n\rangle + |m\rangle = |p\rangle$$

where by the definition of a vector space, $|p\rangle$ is a member of the vector space. There are also a bunch of other properties that the vectors in these vector spaces have, such as associativity, the definition of an inner/scalar product, etc. Then we have operators, which act on vectors in our vector space, and return another vector:

$$\hat{Q}\,|n\rangle = |m\rangle$$

Classical mechanics deals with phase space, in 1D we have two variables, position and momentum in a single direction. Newton's Laws tell us that $\frac{dp_x}{dt} = F_x \to p_x(t) = p_x(0) + \int F_x\,dt$. We also have from the definition of momentum $p_x = mv_x \to \frac{p_x}{m} = \frac{dx}{dt} \to x(t) = x(0) + \int \frac{p_x(t)}{m}\,dt$. We see that we know everything that happens at any time if we know the starting conditions and all the forces. Thus the vector formed by x and p_x represents the state of the system.

In quantum mechanics, we still have a statevector, such as $|S(t)\rangle$, which has name S and depends on the variable t, and is a vector via the braket notation. This represents the state of a quantum system. In quantum mechanics, variables like x and p have operators $\hat{x}$ and $\hat{p}$, and all physical properties (measurable things) also have operators. For example, L, the angular momentum, has an operator that is a function of the operators for position and momentum. This is known as canonical quantization, the replacement of the variables with the operators that represent them. Other operators are things like intrinsic spin, $\hat{s}$, which has no spatial dependence (for an electron).

Also note that operating with something like $\hat{x}$ does not return the value of x. We have a Hamiltonian operator $\hat{H}$, which is the total energy operator. $|S(t)\rangle$ evolves in time via

$$\hat{H}\,|S(t)\rangle = i\hbar\frac{\partial}{\partial t}\,|S(t)\rangle$$

This relationship holds because it matches what we expect, it isn't something that we have derived from mathematics or pure physical laws, we use it because it works.

Every physical quantity q has an operator $\hat{Q}$. The operator $\hat{Q}$ has eigenstates $|q\rangle$, for which the following relationship is true

$$\hat{Q}\,|q\rangle = q\,|q\rangle$$

Note that we can either have a discrete set of eigenstates or continuous set of eigenstates. For example, systems such as the particle in a box or a hydrogen atom has a discrete list of possible energy measurements. Meanwhile, measuring something like the position of a free particle can return a continuous set of eigenstates.

Also note that the eigenvalues must be real, as the operators represent physical measurables.

We also have that the eigenstates are orthogonal (or can be made orthogonal), normalizable and complete. Our proof for completeness is that if they weren't complete, the physics wouldn't make sense and therefore it must form a basis:

$$|S(t)\rangle = \sum_q a_q(t)\,|q\rangle$$

The probability comes into play when we attempt to measure $\hat{Q}$. This will return one of the eigenvalues, with probabilities given by the magnitude of the coefficient:

$$P(q) = |a_q(t)|^2$$

Suppose we have some vector $\mathbf{A}$ on a 2D plane. We can break this down into components and find $\mathbf{A}_x$ and $\mathbf{A}_y$. However, we could also use a different coordinate system, and we could find $\mathbf{A}'_x$ and $\mathbf{A}'_y$. We could do this for any basis that we wanted. We know from linear algebra that finding the components is given by taking the dot product with the unit vector in the direction that we want. This same principle holds true in quantum mechanics.

Suppose we wanted to represent $|S(t)\rangle$ in the position basis (1D). We can dot the state with the unit vector in that direction:

$$\Psi_S(x,t) = \langle x|S(t)\rangle$$

and this gets us the time and position dependent wavefunction for the state. For momentum:

$$\Phi_S(p,t) = \langle p|S(t)\rangle$$

0.2 Operators and Changing Bases

Operators are just things that map from objects in our space to other objects in our space:

$$|\beta\rangle = \hat{Q}\,|\alpha\rangle$$

We are generally working in an orthogonal and normalized basis, where the basis vectors are discrete, $|e_n\rangle$. We can expand out each of our kets:

$$|\alpha\rangle = \sum_n a_n\,|e_n\rangle \quad |\beta\rangle = \sum b_n\,|e_n\rangle$$

We can then substitute them into our operator expression:

$$\sum b_n\,|e_n\rangle = \sum \hat{Q}a_n\,|e_n\rangle$$

Now using the orthogonality of the basis, we can dot both sides with $\langle e_m|$:

$$b_m = \sum a_n\,\langle e_m|\hat{Q}|e_n\rangle$$

We see that we have found the component in the m direction of the ket $|\beta\rangle$. We also see that $\langle e_m|\hat{Q}|e_n\rangle = Q_{mn}$, a matrix element of the matrix representation of the $\hat{Q}$ operator. Also note that from this, we have that $\hat{Q}$ must be square.

When we have an inner product $\langle f|g\rangle$, and there are two main ways of going about computing it. The definition of this inner product is given by

$$\langle f|g\rangle = \int f^*(x)g(x)\,dx$$

This works for continuous variables, but what if we have discrete vectors? In this case, the bra is a row vector, with conjugated elements, and then a ket is given by a column vector. Thus when we compute the inner product:

$$\langle f|g\rangle = f_1^*g_1 + f_2^*g_2 + \dots$$

If we compare these two, we see that via the definition of an integral, the integral method is just a continuous version of the discrete sum, and the two processes are identical.

Let us define something that we claim is an operator:

$$\hat{P}_\alpha = |\alpha\rangle \langle\alpha|$$

Suppose this operates on $|\alpha\rangle$:

$$\hat{P}_\alpha |\alpha\rangle = |\alpha\rangle \langle\alpha| |\alpha\rangle = |\alpha\rangle$$

We see that this takes a vector to a vector. Suppose we have it operate on an arbitrary vector $|\beta\rangle$:

$$\hat{P}_\alpha |\beta\rangle = |\alpha\rangle \langle\alpha|\beta\rangle = \langle\alpha|\beta\rangle |\alpha\rangle$$

We can see that $\langle\alpha|\beta\rangle$ is the amount of $|\beta\rangle$ in the $|\alpha\rangle$ direction.

This is known as the projection operator.

We can define another operator:

$$\sum \hat{P}_n = \sum_n |e_n\rangle \langle e_n|$$

If we think about this, we see that this is just the identity operator, it does nothing to a vector:

$$\left(\sum \hat{P}_n\right) |\alpha\rangle = |\alpha\rangle$$

We can define a continuum version:

$$\int |x\rangle \langle x| \, dx = \mathbb{1}$$

Suppose we have an abstract state $|S(t)\rangle$:

$$|S(t)\rangle = \mathbb{1} |S(t)\rangle = \int dx \; |x\rangle \langle x|S(t)\rangle$$

Now we look at the inner product, and we see that this is just $\Psi(x,t)$:

$$|S(t)\rangle = \int dx \; \Psi(x,t) |x\rangle$$

We can do the same thing in the momentum basis:

$$|S(t)\rangle = \int dp \; \Phi(p,t) |p\rangle$$

This is the basis for the Fourier Transform.

Let us now apply this identity operator. We can talk about spin-$\frac{1}{2}$ particles, as well as combining angular momenta.

Suppose we have a momentum space wavefunction:

$$\Psi(p,t) = \langle x|S(t)\rangle$$

If we want to find $\Phi(p,t) = \langle p|S(t)\rangle$, We can use the fact that the identity operator is given by

$$\mathbb{1} = \int dx \; |x\rangle \langle x|$$

And we can plug this into our inner product:

$$\langle p|S(t)\rangle = \langle p| \int dx\ |x\rangle \langle x|\ S(t)\rangle$$

$$= \langle p| \int dx\ |x\rangle\ \Psi(x,t)\rangle = \int dx\ \langle p|x\rangle\ \Psi(x,t)$$

The inner product $\langle p|x\rangle$ is the position eigenfunction in the momentum basis. We can flip this using the property that you have to complex conjugate it:

$$= \int dx\ \langle x|p\rangle^*\ \Psi(x,t)$$

Now using the fact that $\langle x|p\rangle^* = \sqrt{\frac{1}{2\pi\hbar}}e^{-ipx}$:

$$\Phi(p,t) = \int dx \sqrt{\frac{1}{2\pi\hbar}} e^{-ipx}\ \Psi(x,t)$$

and we see that we have just derived the Fourier transform.

What if we want to convert from the momentum wavefunction to the energy wavefunction like we did last time, but we put in another identity operator:

$$\Phi(p,t) = \sum \langle p|n\rangle \langle n|S(t)\rangle = \sum_n \langle p \int |x\rangle \langle x|\ dx|n\rangle \langle n|S(t)\rangle$$

$$= \sum_n \int \langle p|x\rangle \langle x|n\rangle \langle n|S(t)\rangle$$

We know that $\langle x|n\rangle = \psi_n(x)$, and $\langle n|S(t)\rangle = c_n$:

$$= \sum \int \langle x|p\rangle^*\ \psi_n(x) c_n = \sum_n \int \sqrt{\frac{1}{2\pi\hbar}} e^{-ipx/\hbar} \psi_n(x)\, dx\, c_n$$

Which is the more convential definition of a Fourier transform.

What is $\hat{x}$ in the p basis? We have our state $S(t)$, and we want to be in the p basis, so we set up something like:

$$\langle p|\hat{X}|S(t)\rangle$$

where $\hat{X}$ is the unknown position operator. We want to use the fact that $\hat{X}\,|x\rangle = x\,|x\rangle$, and then the identity, which we can stick in the second slot:

$$\langle p|\hat{X}|S(t)\rangle = \langle p|\ \hat{X} \int |x\rangle \langle x|\ |S(t)\rangle\ dx$$

$$= \int \langle p|x\rangle\, x\Psi(x,t)\, dx = \int \sqrt{\frac{1}{2\pi\hbar}} e^{-ipx/\hbar} x\Psi(x,t)\, dx$$

Now we note that the partial with respect to p of $e^{-ipx/\hbar} = -\frac{ix}{\hbar}e^{-ipx/\hbar}$.

0.3 Bloch Sphere

When talking about spin, we have to think about the direction, and the convention is to use:

$$|\uparrow\rangle_z = \chi_+^z \quad |\downarrow\rangle_z = \chi_-^z$$

We have that we can use the z direction spins to form the x direction spin, and the same for the y direction.

$$\chi_\pm^x = \frac{1}{\sqrt{2}}\left(\chi_+^z \pm \chi_-^z\right)$$
$$\chi_\pm^y = \frac{1}{\sqrt{2}}\left(\chi_+^z \pm i\chi_-^z\right)$$

We want to work towards something known as the Bloch sphere.

What is the most general state that we can write in the z basis:

$$\chi = a\chi_+^z + b\chi_-^z$$

We have to constrain a and b in order to make this physically realisable, and we need $|a|^2 + |b|^2 = 1$, to make the probability equal to 1. In general, we have that

$$a = |a|e^{i\gamma_a}$$

and similarly for b.

We can write out the general state:

$$\chi = e^{i\gamma_a}\left(|a|\chi_+^z + |b|e^{i(\gamma_b - \gamma_a)}\chi_-^z\right)$$

WLOG, we can set $\gamma_a = 0$, because we only care about the phase difference between the two, now that we've factored it out, its an overall phase factor that doesn't affect the total state.

Bloch then constructs a state where

$$|a| = \cos\frac{\theta}{2} \quad |b| = \sin\frac{\theta}{2}$$

and where $\gamma_b - \gamma_a = \varphi$. We can write out the general state now:

$$\chi = \cos\frac{\theta}{2}\chi_+^z + \sin\frac{\theta}{2}e^{i\varphi}\chi_-^z$$

Note that this is a constructed state. Suppose we choose $\theta = 0$, we notice that we are left with just the up spin. If we instead choose $\theta = \pi$, we have the down spin. We see that rotation by π switches us from up spin to down spin.

Suppose we choose $\theta = \frac{\pi}{2}$. We see that we have

$$\chi = \frac{1}{\sqrt{2}}\left(\chi_+^z + e^{i\phi}\chi_-^z\right) = \chi_+^x$$

We see that rotating halfway has now put us in the x spin direction. If we rotate from here and change ϕ to π, which then changes the sign of the second term, and gives us χ_-^x. Bloch mapped the modifications to θ and ϕ to spherical coordinates. If we have some general state, we can define it using its θ and its ϕ. Since everything is normalized, we have that our states live on the surface of a sphere, which is known as the Bloch sphere.

0.4 When Hilbert Spaces Collide

Suppose we have two spin-$\frac{1}{2}$ particles that are interacting, how do we deal with that. The classical example is angular momentum states.

We have some particle in state $|S_1, m_1\rangle$. This is a state with total angular momentum characterized by the quantum number S_1.We have a total spin operator:

$$S^{(1)^2} |S_1, m_1\rangle = S_1(S_1+1)\hbar^2 |S_1, m_1\rangle$$

We can also do it in a certain direction:

$$S_z^{(1)} |S_1, m_1\rangle = m_1\hbar |S_1, m_1\rangle$$

Where the superscript denotes the particle that we are looking at.

In the Bohr orbit model (Bohrbit), we had some quantized angular momentum $\mathbf{L}_n$.

We can talk about particle number 2 having the same properties:

$$S^{(2)^2} |S_2, m_2\rangle = S_2(S_2+1)\hbar^2 |S_{2,2}\rangle$$

$$S_z^{(2)} |S_2, m_2\rangle = m_2\hbar |S_2, m_2\rangle$$

How do we define the composite state of these two? The composite state is labelled:

$$|S_1, S_2, m_1, m_2\rangle$$

This state has to obey certain rules, the rules given for both states individually must hold for the final state:

$$S^{(1)^2} |S_1, S_2, m_1, m_2\rangle = S_1(S_1+1)\hbar^2 |S_1, S_2, m_1, m_2\rangle$$
$$S^{(2)^2} |S_1, S_2, m_1, m_2\rangle = S_2(S_2+1)\hbar^2 |S_1, S_2, m_1, m_2\rangle$$
$$S_z^{(1)} |S_1, S_2, m_1, m_2\rangle = m_1\hbar |S_1, S_2, m_1, m_2\rangle$$
$$S_z^{(2)} |S_1, S_2, m_1, m_2\rangle = m_2\hbar |S_1, S_2, m_1, m_2\rangle$$

If we add the last two equations:

$$(S_z^{(1)} + S_z^{(2)}) |S_1, S_2, m_1, m_2\rangle = (m_1+m_2)\hbar |S_1, S_2, m_1, m_2\rangle$$

We tentatively call this new operator S_z.

From now on, we let $S_1 = \frac{1}{2}$, and $S_2 = \frac{1}{2}$, we leave the general case and restrict it to two spin-1/2 particles. This gets us that $m_1 = \pm 1/2$ and $m_2 = \pm 1/2$.

We can then represent the system schematically as

$$|\uparrow\uparrow\rangle \quad |\uparrow\downarrow\rangle \quad |\downarrow\uparrow\rangle \quad |\downarrow\downarrow\rangle$$

We can now make some guesses, and for the first state we say that since $m_1 = m_2 = 1/2$, $m = 1$. Similarly, for the last state, we have that $m_1 = m_2 = -1/2$, and thus $m = -1$. For the middle two states, we have that $m = 0$. However, when $m = 0$, what is the value of S? Is it 0 or is it 1 like

the other states? We have another operator that we can use, the ladder operators for the angular momentum:

$$S_\pm \left|S, m\right\rangle = \hbar\sqrt{S(S+1) - m(m+1)}\left|S, m \pm 1\right\rangle$$

We can apply the raising and lowering operators to the composite states:

$$S_-^{(1)}\left|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right\rangle = \hbar\left|\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, \frac{1}{2}\right\rangle$$

$$S_-^{(2)}\left|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right\rangle = \hbar\left|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, -\frac{1}{2}\right\rangle$$

We also have the S_z operator:

$$S_z^{(1)}\left|\frac{1}{2}, \frac{1}{2}, m_1, m_2\right\rangle = m_1\hbar\left|\frac{1}{2}, \frac{1}{2}, m_1, m_2\right\rangle$$

If we add the usage of the lowering operators on both particles:

$$(S_-^{(1)} + S_-^{(2)})\left|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right\rangle = \hbar\left(\left|\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, \frac{1}{2}\right\rangle + \left|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, -\frac{1}{2}\right\rangle\right)$$

If we operate the lowering operator again on this state:

$$(S_-^{(1)} + S_-^{(2)})\hbar\left(\left|\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, \frac{1}{2}\right\rangle + \left|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, -\frac{1}{2}\right\rangle\right) = 2\hbar^2\left|\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}\right\rangle$$

We see that

$$(S_-^{(1)} + S_-^{(2)})^2\left|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right\rangle = 2\hbar^2\left|\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}\right\rangle$$

We can define 3 new states:

$$\left|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right\rangle = |1, 1\rangle$$

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

$$\left|\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}\right\rangle = |1, -1\rangle$$

We have to show that $S^2 = [S^{(1)} + S^{(2)}]^2\left|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right\rangle = S(S+1)\hbar^2\left|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right\rangle$.

These are known as triplet states:

$$|1, 1\rangle = |\uparrow, \uparrow\rangle \quad |1, 0\rangle = \frac{1}{\sqrt{2}}(|\uparrow, \downarrow\rangle + |\downarrow, \uparrow\rangle) \quad |1, -1\rangle = |\downarrow, \downarrow\rangle$$

More compactly, we have $S = 1$, and varied $m = 1, 0, -1$. We need another state, which we can construct:

$$\frac{1}{\sqrt{2}}(|\uparrow, \downarrow\rangle - |\uparrow, \downarrow\rangle)$$

This is called the singlet state, and it has the property that the total spin is 0, $S = 0$ and $m = 0$.

We can generate any general composite state $|s, m\rangle$:

$$|s, m\rangle = \sum_{m_1+m_2=m} C^{s_1,s_2,s}_{m_1,m_2,m} |s_1, s_2, m_1, m_2\rangle$$

Where C represents the Clebsh-Gordan coefficients, which can be read from a table.

We can also represent these composite states using a schematic vector addition diagram, one a 3-d sphere with axes being each spin direction.

1 Identical Particles

In atomic potentials, we deal a lot with central potentials, and we can also talk about non-interacting particles, such as bosons and fermions. We can also talk about exchange interactions, which is when non-interacting particles such as fermions and bosons still exhibit properties regarding their states with each other.

We can write out the classical H for a particle with some potential $V(\mathbf{r})$:

$$H = \frac{|\mathbf{p}|^2}{2m} + V(\mathbf{r})$$

And we can write out the momentum operator:

$$\hat{p} = \frac{\hbar}{i}\nabla$$

We can put this together to get the quantum Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})$$

How would we extend this to a second particle in the same system?

We add the kinetic energies, and we claim that the potential will be some function of the two positions.

$$H = \frac{|\mathbf{p}_1|^2}{2m_1} + \frac{|\mathbf{p}_2|^2}{2m_2} + V(\mathbf{r}_1, \mathbf{r}_2)$$

Converting this to the quantum operator:

$$\hat{H} = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\mathbf{r}_1, \mathbf{r}_2)$$

Where $\nabla_j^2 = \frac{\partial^2}{\partial x_j^2} + \frac{\partial^2}{\partial y_j^2} + \frac{\partial^2}{\partial z_j^2}$. We can write down the Schrodinger equation:

$$\left(-\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2\right)\Psi(\mathbf{r}_1, \mathbf{r}_2, t) + V(\mathbf{r}_1, \mathbf{r}_2)\Psi = i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}_1, \mathbf{r}_2, t)$$

We can attempt to do the separation of variables that we did the first time we looked at this equation:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \psi(\mathbf{r}_1, \mathbf{r}_2)\Phi(t)$$

If we insert this into the equation, and then separate this into two equations,

$$i\hbar\frac{\partial\Phi(t)}{\partial t} = E\Phi(t)$$

$$-\frac{\hbar^2}{2}\left(\frac{\nabla_1^2}{m_1}+\frac{\nabla_2^2}{m_2}\right)\psi+V\psi=E\psi$$

Solving the Φ equation:

$$\Phi(t)=e^{-iEt/\hbar}$$

We see that we have the same thing as the one-particle result.

For a special case, $V(\mathbf{r}_1,\mathbf{r}_2)=V(\mathbf{r}_1)+V(\mathbf{r}_2)$. We are essentially saying that there is no interaction between the two particles, there is no crossterm. We write down that

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)$$

We can do separation of variables on this, and we find that

$$\left[-\frac{\hbar^2}{2m_1}\nabla_1^2+V(\mathbf{r}_1)\right]\psi_a(\mathbf{r}_1)=E_a\psi_a(\mathbf{r}_1)$$

$$\left[-\frac{\hbar^2}{2m_2}\nabla_2^2+V(\mathbf{r}_2)\right]\psi_b(\mathbf{r}_2)=E_b\psi_b(\mathbf{r}_2)$$

We have two separate Schrodinger equations. We can put together the overall wavefunction:

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,t)=\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)e^{-iEt/\hbar}$$

Where $E=E_a+E_b$. This is a solution because the Schrodinger equation is linear. Suppose we have a state

$$\Psi=\frac{3}{5}\psi_a(\mathbf{r}_1)e^{-iE_at/\hbar}\psi_b(\mathbf{r}_2)e^{-iE_bt/\hbar}+\frac{4}{5}\psi_c(\mathbf{r}_1)e^{-iE_ct/\hbar}\psi_d(\mathbf{r}_2)e^{-iE_dt/\hbar}$$

What if we measure the energy of particle 1 and get E_a, and then measure the energy of the second particle, we see that we must get E_b, because the measurement collapsed it to the first term.

This is what lead to the idea of entanglement, where measuring one particle instantly gives information about the second particle. This does not violate relativity, since we cannot use it to signal faster than the speed of light.

To recap, we took the Schrodinger equation for two particles, with time dependence, and then separated variables to get a time-independent equation. We then separated again, to get two Schrodinger equations, each for the wavefunction of a single particle, with no time dependence.

Suppose the particles exist in the same harmonic oscillator potential. If we suppose that ψ_a is the ground state, and ψ_b is the first excited state, and we do a measurement, and we find that the particle is at some x value. Note that we said "the" particle, because we don't know which one it is. We have some detector that beeps at that particular position, but we have no way of knowing which one we measured. This is different from the classical case, where we know about the position and momenta of both particles or objects, since the previous state can predict the future state with perfect accuracy.

However, since we have two Gaussian packets representing the two particles, when the two are really far from each other, we can pretty easily label each particle, but after they interact, we cannot tell them apart. This is forced upon us by the statistical nature of the quantum states.

Gibbs noted this around 1874, where he realized that using indistinguishable particles in his classical model of the ideal gas was the only way to get correct results, something known as the Gibb's paradox.

if they are indistinguishable, then writing

$$\psi_a(\mathbf{R}_1)\psi_b(\mathbf{r}_2)$$

is no good, because this is explicitly distinguishable.

We can instead write it out using linear combinations:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = A\left[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \alpha\psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)\right]$$

And we also claim that

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\psi(\mathbf{r}_2, \mathbf{r}_1)|^2$$

This set of two equations implies two things:

$$|\alpha|^2 = 1 \quad \alpha = \alpha^*$$

This tells us that $\alpha = \pm 1$.

There are only two things that are allowed:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = A\left[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \pm \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)\right]$$

This relationship actually leads to the difference between bosons and fermions. If we first look at the $-$ states, and we let $a = b$, we have them in the same state

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = 0$$

We see that we have the Pauli exclusion principle, we can't have Fermions in the same state, the states cancel out and the wavefunction is 0. If we instead look at the Bosons, they add, and the wavefunction is nonzero.

If the particles are distinguishable, we can just use a product state. For these "distinguishons":

$$\Psi_d(x_1, x_2, t) = \psi_a(x_1, t)\psi_b(x_2, t)$$

For Fermions:

$$\Psi_F(x_1, x_2, t) = \psi_a(x_1, t)\psi_b(x_2, t) - \psi_a(x_2, t)\psi_b(x_1, t)$$

And for Bosons:

$$\Psi_B(x_1, x_2, t) = \psi_a(x_1, t)\psi_b(x_2, t) + \psi_a(x_2, t)\psi_b(x_1, t)$$

where we have dropped the normalization constants.

We can take an expectation value:

$$\langle (x_1 - x_2)^2 \rangle$$

And we can do tis for 3 different cases, distinguishable particles, Fermions, and Bosons. This is like a measure of how far apart the particles are on average. We find that for distinguishable particles:

$$\langle (x_1 - x_2)^2 \rangle_d = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b$$

Where we can drop the particle state labels because x is just a variable that we are integrating over.

For Bosons and Fermions:

$$\langle (x_1 - x_2)^2 \rangle = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b \mp | \langle x \rangle_{ab} |^2$$

Where $\langle x \rangle_{ab} = \int x \psi_a^*(x) \psi_b(x)\, dx$. We see that we have an added term to the Distinguishon case. This extra term is sometimes called an overlap integral, because its based on whether the wavefunctions are overlapping, otherwise it is 0. If the two are very far apart, we see that we can indeed point out the two particles, just like the distinguishable case. If there is an overlap, it may be a nonzero term. We see that this adds the idea of an iteraction between particles, the Fermions repel while the Bosons attract each other. This is sometimes called the exchange force, but it's not really a Newtonian force.

So far, we have considered only the spatial part of the state function. We also need to look at the spinor:

$$\begin{pmatrix} a(t) \\ b(t) \end{pmatrix} = \chi(t)$$

Where a and b represent the time evolution of spin up and spin down respectively.

Thus what we really care about is ($+$ is Bosons, and $-$ is Fermions):

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t)\chi(1, 2, t) = \pm \Psi(\mathbf{r}_2, \mathbf{r}_1, t)\chi(2, 1, t)$$

Recall that when we looked at the spin 1/2 particle angular-momentum states (the triplet states), we see that if we swap the particle spins, then we have no change, the triplet states are even. If we have the singlet state, we see that flipping the spins gives the same state but with an added sign change. Since Fermions are spin-1/2, we have to get a $-$ out somewhere. Either the spin part or the spatial part must provide the sign. For the triplet states, the spatial part must provide the sign, and for the singlet state, the spin state must provide the negative.

2 Atoms

We can write out our Hamiltonian:

$$\hat{H} = \sum_j^N \left[\frac{\hbar^2}{2m} \nabla_j^2 - \frac{(Z_e)(e)}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_j|} \right]$$

Where the sum over j is summing over all electrons, and the second term is the Coulomb interaction, Z is atomic number.

We can now do the interaction term:

$$\sum_{i=1}^N \sum_{j=1, j\neq i}^N \frac{1}{2} \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Where the $\frac{1}{2}$ removes double counting, and we remove self-interactions using the fact that $j \neq i$.

$$\hat{H} = \sum_j^N \left[\frac{\hbar^2}{2m} \nabla_j^2 - \frac{(Z_e)(e)}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_j|} \right] + \sum_{i=1}^N \sum_{j=1, j\neq i}^N \frac{1}{2} \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

We can still separate out the Schrodinger equation:

$$\hat{H}\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = E\psi$$

We begin by ignoring the electron-electron interaction term for now. We define $\hat{H}_0$ as the Hamiltonian ignoring the interactions. We can do this for Helium:

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{|\mathbf{r}_1|(4\pi\epsilon_0)} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{|\mathbf{r}_2|(4\pi\epsilon_0)}$$

We can once again separate variables, and we have that $E = E_n + E_{n'}$.

When we solved the Hydrogen atom, we found that

$$E_n = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{1}{n^2}$$

Switching this to Helium, we know that e^2 goes to $2e^2$ for both electrons:

$$E_{n,n'} = -\frac{m}{2\hbar^2}\left(\frac{2e^2}{4\pi\epsilon_0}\right)^2 \frac{1}{n^2} - \frac{m}{2\hbar^2}\left(\frac{2e^2}{4\pi\epsilon_0}\right)^2 \frac{1}{n'^2}$$

We see that we have just two hydrogen energies put together, with a changed term on the inside.

We guess that the lowest state is $n = n' = 1$. We find that $E_{1,1} = 8 \times -13.6$ eV, which is -109 eV. The experimental value for this is -78.975 eV. We have ignored the fact that the electrons interact with each other, which causes the difference from the experimental value. Constructing the interaction term:

$$\frac{1}{4\pi\epsilon_0}\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

The first thought is to plug in a "typical" value for the difference of the vectors. For Hydrogen, this would be the Bohr radius:

$$a = \frac{4\pi\epsilon_0}{me^2} = 0.529\text{Å}$$

If we now insert in $2e^2$ instead of e^2, we have that the Bohr radius for Helium would be $\tilde{a} = 0.264$Å. Plugging this into the interaction term, we have that $\Delta E_{ee} = 54.4$ eV. Adding this to the value we computed for $E_{1,1}$, we find -54.6 eV. Thus we see we've overcompensated, the Bohr radius is not a good typical value.

Instead, let us use the average interaction:

$$\left\langle \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\rangle$$

Pulling the constants out:

$$= \frac{e^2}{4\pi\epsilon_0}\left\langle \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\rangle$$

If we use this, we find that $E_{1,1} = -75$ eV, compared to the experimental -78.975 eV.

We have the Hydrogen state functions, with just the spatial component:

$$\psi(r, \theta, \varphi) = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n(n+l)}} e^{-r/na}\left(\frac{2r}{na}\right)^l \left[L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)\right] Y_l^m(\theta, \varphi)$$

Where L are the associated Laguerre polynomials, and Y are spherical harmonics.

And the energies are given by

$$E_n = -\frac{13.6}{n^2}$$

We have a Bohr radius:

$$a = \frac{4\pi\varepsilon_0\hbar^2}{me^2}$$

These functions are the energy eigenfunctions:

$$\hat{H}\psi_{nlm} = E_n\psi_{nlm}$$

And also eigenfunctions of angular momentum:

$$\hat{L}^2\psi_{nlm} = l(l+1)\hbar^2\psi_{nlm}$$

$$L_Z\psi_{nlm} = m\hbar\psi_{nlm}$$

We also have to incorporate the fact that $S_z = \pm\frac{1}{2}\hbar$. We have that $l = 0, 1, 2, \ldots, n-1$ and we have that $m = -l, -l+1, \ldots, 0, 1, \ldots, l$.

We have seen that Helium has $Z = 2$, and that we can separate the variables into two different wavefunctions, if we ignore the electron-electron interaction. We saw that this didn't get us that bad of a result, so for atoms in general:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_Z) = \prod_{j=1}^{Z} \psi_{n_j,l_j,m_j}(\mathbf{r}_j)$$

We have to fiddle with these so if we swap $\mathbf{r}_q$ and $\mathbf{r}_s$, we have to negate the wavefunction, since the particles we're dealing with are Fermions.

We have $2l+1$ different distinct values of m, and there are n values of l. For a fixed n, we have a lot of degenerate states. And we have 2 for spin up and spin down.

For fixed n, we have $2n^2$ degenerate states (states with the same energy). For $n = 1$, we have Hydrogen and Helium, and for $n = 2$, we need 8 to fill up the shell ($2n^2$ degenerate states). This leads us up to Neon.

If we follow this, we predict 18 atoms until the next Noble gas, but we need only 8. The reason for this is that it is more energetically favorable to skip spots in one of the shells.

3 Solids

We will be looking at the electronic properties, and we will assume that we know the crystal structure, and we have N electrons. We will also assume that there are d outer shell electrons, that are weakly bound.

The outer shell electrons (Nd of them) delocalize. This means that they are free to move around. Instead of dealing with the ionic cores, let us smear the ions out, making it a uniform sort of "pudding" of positive charge, with the electrons moving around. This is known as the jellium model. If we zoom in on some electron, it repulses all other electrons, and pulls the ionic cores slightly.

This gets a small region around the electron with net positive charge. It can be shown that the potential between any two electrons

$$V_{12} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_{12}}\exp -\frac{|\mathbf{r}_{12}|}{\lambda_{TF}}$$

Where λ_{TF} is known as the Thomas-Fermi length. We essentially have the Coloumb force with a "screen" term tacked on. It can be shown that $\lambda_{TF} \propto \left(\frac{1}{\rho}\right)^{1/3}$, where ρ is the number of electrons per unit volume, the charge density. The fact that an electron does not really feel the other electrons in the gas is due to the fact that we have a "screened" Coulomb potential. Generally, we can start out by neglecting the $e-e$ interaction because it is effectively weak.

We have our jellium positive charge, with our screened electrons. We have no net charge over the entire jellium. If we kick out an electron, that generates a missing electron where the electron was. This missing electron generates a Coloumb force, which is the reason that electrons don't just leave materials, since the Colomb force is strong. This generates a 3D box potential. We have a box of size l_x, l_y, and l_z, and we have N ions and Nd electrons. Note that we don't have to do a box potential, we could instead use periodic boundary conditions or anti-periodic boundary conditions, and they will lead to the same result.

We have that the wavefunction splits into 3 directions:

$$\Psi(x,y,z) = X(x)Y(y)Z(z)$$

And if we go through and solve this, doing 2 separation of variables on the Schrodinger equation:

$$\Psi(x,y,z) = \sqrt{\frac{8}{l_x l_y l_z}}\sin k_x x \sin k_y y \sin k_z z$$

Where $k_x = \frac{n_x\pi}{l_x}$, for $n_x = 0,1,2,\ldots$, and similarly for k_y and k_z. The energy is given by

$$E = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$$

Let us set ourselves into the 1 dimensional case. In this case, $\psi(x) = \sqrt{\frac{2}{l}}\sin\frac{n_x\pi x}{l_x}$. These are standing waves on a string. The energies are given by $E = \frac{\hbar^2}{2m}\frac{\pi^2}{l_x^2}n_x^2$. We can fit 2 electrons into each energy level (1 spin up and 1 spin down). Note that the reason we cannot fit more than 2 is that we are only in 1 dimension, we only have 2 quantum numbers, n_x and the spin.

What if we wnat to find the ground state energy? We have to begin with what $n_{x_{max}}$. If we have Nd electrons, since we can fit 2 electrons into each energy level, we have that $n_{max} = \frac{Nd}{2}$. We also sometimes call this n_{Fermi}. We now want to find the energy of the maximum energy:

$$E_{\text{Fermi}} = \frac{\hbar^2}{2m}\frac{\pi^2}{l_x^2}\frac{N^2d^2}{4} = \frac{\hbar^2}{2m}\left(\frac{\pi}{2}\right)^2\rho^2$$

We can find the total ground state energy for the 1D electron gas:

$$E_0 = 2(E_1 + E_2 + \cdots + E_F)$$

Instead of doing this, we can find the density of states along the line the system forms in n space, which is 1. We can change the sum to an integral very carefully. We have that our energy is

$$\sum k_n = k_1^{k_F} 2\frac{\hbar^2 k_n^2}{2m} = \int_0^{k_F} \frac{1}{\frac{\pi}{l_x}} 2\frac{\hbar^2 k^2}{2m}$$

Where the two is for the spin factor, and the scaling term is because of the density of states along the k space line. We can compute this:

$$E_0 = 2\frac{l_x}{\pi}\frac{\hbar^2}{2m}\frac{k_F^3}{3}$$

Turns out that we can rewrite this as

$$E_0 = \frac{1}{3}NdE_F$$

In 3D, we still have Nd free electrons. We have that the energy will be given by

$$E = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2}{2m}\left(\left(\frac{n_x\pi}{l_x}\right)^2 + \left(\frac{n_y\pi}{l_y}\right)^2 + \left(\frac{n_z\pi}{l_z}\right)^2\right)$$

We have our Fermi surface, a surface of constant energy that is governed by the variables n_x, n_y, and n_z. While we really care about integer points only, but if N is large, we don't see the jagged nature of the sphere, we can just say the values for the ns are continuous. Also note that we care about only 1 octant of the sphere, otherwise we'll overcount. We have that the total number of electrons, Nd, is equal to

$$Nd = 2\frac{1}{8}V_{n_f}1$$

Where the 2 is due to spin, the $\frac{1}{8}$ for not overcounting, V_{n_f} is the volume of a sphere of radius n_f, and the 1 is the density of states. This leads to the result:

$$k_f = \left(3\pi^2\frac{Nd}{V}\right)^{1/3}$$

Inserting this into the expression for E_f:

$$E_F = \frac{\hbar^2}{2m}\left(3\pi^2\frac{Nd}{V}\right)^{2/3}$$

From this, we can find the total ground state energy:

$$E_0 = \frac{3}{5}NdE_f$$

Suppose that we have a cube of length l, and we expand it by some amount $V \to V + \Delta V$. We see that the ground state energy will change, because E_f is dependent on V. We have some ΔE_0:

$$\Delta E_0 = E_0\left(-\frac{2}{3}\right)\frac{\Delta V}{V}$$

From this, we can find the fractional change:

$$\frac{\Delta E_0}{E_0} = -\frac{2}{3}\frac{\Delta V}{V}$$

For a classical gas, we would say that

$$\Delta E = \Delta W = F\Delta x = -P\Delta V$$

Where W is the work done **by** the system. Thus we have that

$$\frac{\Delta E}{E_0} = -\frac{2}{3}\frac{\Delta V}{V} = -\frac{P\Delta V}{E_0} \to P = \frac{2}{3}\frac{E_0}{V}$$

This is the pressure of an electron gas. This is the effect of the Pauli Exclusion principle and the Heisenberg Uncertainty Principle.

We can also look at the electrical conductance of a material. We can first talk about probability. We have that the total probability is equal to 1, and is conserved over the infinite region. Suppose we instead look at a finite region. We can define something known as the probability current, which defines how the probability at a certain point changes over time:

$$J_p(x,t) = \frac{i\hbar}{2m}\left(\Psi(x,t)\frac{\partial \Psi^*(x,t)}{\partial x} - \Psi^*(x,t)\frac{\partial \Psi(x,t)}{\partial x}\right)$$

The electrical current (in 1D), is given by $J_{\text{elec}} = -eJ_p$, where e is the charge of an electron. Suppose we have a box, with hard walls, and we have periodic boundary conditions. We can create a current via the application of a time-varying magnetic field $\mathbf{B}(t)$. We have that $\Psi(l) = \psi(0)$. The wavefunction will like a free particle, with a restriction from the boundary conditions:

$$\Psi(x,t) = Ae^{ikx}e^{-ie_k t/\hbar}$$

Where $E_k = \frac{\hbar^2}{2m}k^2$. If we work it all out, we find that

$$J_e = \frac{e}{m}\hbar k\frac{1}{l_x}$$

This indeed has units of charge per unit time, and is a current. If we place this under a electric field, we find that

$$\hbar k = \hbar k(t=0) + -eEt$$

3.1 Effects of Periodic Potential on Electron Gas

We have a lattice of electrons, with some periodic potential, with minima at the positions of the electrons on the lattice. We have a theorem, which states that we have translational symmetry, if $x \to x + na$, where a is the lattice spacing, the physics is the same. Since we cannot measure ψ, only ψ^2:

$$\psi(x+a) = e^{iqa}\psi(x)$$

Using the boundary condition that for a line of N atoms:

$$\psi(0) = \psi(Na)$$

Using the previous statement, we have $e^{iNqa} = 1$, which tells us that $Nqa = 2\pi m$, for $m \in \mathbb{Z}$. This tells us that the allowed values of q are

$$q = \frac{2\pi n}{Na}$$

This theorem is known as the Bloch theorem.

We can attempt to model this potential using finite square wells, or delta functions. We place the positive delta functions between each lattice point, blocking off each electron from the ones next to it. Alternatively, we could place negative delta functions directly under every lattice point.

We have tunnelling happening between every delta barrier. We see that this quickly leads to a ton of reflected and transmitted waves. We can think of the net wavefunction:

$$\psi = Ae^{iqx} + Be^{-iqx}$$

Due to the Bloch theorem, we can just solve this in one unit cell, and use the translational symmetry to get the physics everywhere else. Suppose we have 3 bouncing waves inside our cell, generated by 3 deflections. Let us label them 1,2, and 3. The path length of 1 and 2 is $2a$. If 3 must be in phase with 1, then $2a = n\lambda$, for some integer n, telling us that $\lambda = \frac{2a}{n}$. This is the condition for constructive interference. In one cell, we have

$$\psi = Ae^{iqx} + Be^{-iqx} = (A+B)\cos(qx) + i(A-B)\sin(qx)$$

3.2 Delta Function Scattering

We have that ψ is assumed to be continuous, and we find a boundary condition on $\frac{\partial\psi}{\partial x}$. Starting with the Schrodinger equation:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

We can rewrite this:

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}[V(x) - E]$$

We can integrate both sides from some point $x_0 - \epsilon$ to $x_0 + \epsilon$ to get a relationship for the first derivative

$$\int_{x_0-\epsilon}^{x_0+\epsilon} \frac{d^2\psi}{dx^2}\,dx = \frac{2m}{\hbar^2}\int_{x_0-\epsilon}^{x_0+\epsilon}[V(x) - E]\psi\,dx = \frac{2m}{\hbar^2}2\epsilon[V(x_0) - E]\psi(x_0)$$

Now if we have that $V(x) = \alpha\delta(x - x_0)$:

$$\left(\frac{d\psi}{dx}\right)_{x_0+\epsilon} - \left(\frac{d\psi}{dx}\right)_{x_0-\epsilon} = \frac{2m}{\hbar^2}\psi(x_0)\alpha = \Delta\left(\frac{d\psi}{dx}\right)_{x_0}$$

Now let us use this to go back to solving our periodic potential in the gas. We can look at only one cell, due to the previously stated Bloch theorem, which exploits the discrete translational symmetry of the system. Looking at the cell from $0 \le x \le a$, we have some boundary conditions. The first is that ψ must be continuous. The second is the statement we just derived, at both $x_0 = 0$ and $x_0 = a$. We begin with the solutions to the infinite square well:

$$\psi(x) = A\sin(kx) + B\cos(kx)$$

Taking the derivative, we have that

$$\frac{d\psi}{dx} = k(A\cos kx - B\sin kx)$$

This is continuous at $x = 0$ and $x = a$. To get the boundary conditions at $x = 0$, we can use the Bloch theorem for the cell to the left. We then get the boundary condition (via continuity and Bloch theorem):

$$\psi(x) = e^{iqa}\left[A\sin k(x+a) + B\cos k(x+a)\right]$$

Inserting $x = 0$, we find that

$$B = e^{-iqa} \left[A \cos ka + B \sin ka \right]$$

And now using the derivative boundary condition:

$$Ak - e^{iqa} Ak \cos ka = \frac{2m}{\hbar^2} \alpha B$$

Now using magic, we are left with the transcendental equation

$$\cos(qa) = \cos(ka) + \frac{m\alpha}{\hbar^2 k} \sin ka$$

We let $ka = z$, where z is a dimensionless parameter. We then let $\beta = \frac{m\alpha a}{\hbar^2}$, we are left with

$$\cos(qa) = \cos(z) + \frac{\beta}{z} \sin z$$

4 Iterative Solutions: Perturbation Theory

Suppose we have some Hamiltonian which is the sum of two different Hamiltonians:

$$\hat{H} = \hat{H}^0 + \hat{H}^1$$

Now suppose that one of the sub-Hamiltonians is known and solvable ($\hat{H}^0$), and the other is not solvable ($\hat{H}^1$).

We have the energy eigenfunctions of the Hamiltonian that we can solve:

$$\hat{H}^0 \left| \psi_n^0 \right\rangle = E_n^0 \left| \psi_n^0 \right\rangle$$

Since the eigenfunctions are orthonormal:

$$\langle \psi_n^0 | \psi_n^0 \rangle = 1 \quad \langle \psi_i^0 | \psi_j^0 \rangle = \delta_{i,j}$$

And since the states are complete:

$$|\phi\rangle = \sum c_i \left| \psi_i^0 \right\rangle \text{ or } \sum_n \left| \psi_n^0 \right\rangle \left\langle \psi_n^0 \right| = \hat{1}$$

for any $|\phi\rangle$.

Let us now write down the full Schrodinger equation:

$$\hat{H} \left| \psi_n \right\rangle = E_n \left| \psi_n \right\rangle$$

Now let us drop the kets for a while, and the hats, since this is extra notational fluff. Let us also say, for bookkeeping purposes, that $H = H^0 + \lambda H^1$, where $0 < \lambda \leq 1$. Our full Schrodinger equation is

$$H\psi_n = E_n \psi_n$$

We now make the following ansatz, which is to assume that we can do something analogous for the wavefunction:

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots$$

Note that the exponents on the ψs are labels, not powers, but the exponents on the λs are powers. More generally:

$$\psi_n = \sum_{j=0}^{\infty} \lambda^j \psi_n^j$$

Note that if we let $\lambda = 0$, where the Hamiltonian is just the unperturbed Hamiltonian, we return to the solution of the solvable Hamiltonian. Now for the energy:

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots$$

Now putting this all together into the Schrodinger equation:

$$(H^0 + \lambda H^1)(\psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \dots) = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots)(\psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \dots)$$

If we restrict this to the second order terms:

$$H^0\psi_n^0 + \lambda(H^1\psi_n^0 + H^0\psi_n^1) + \lambda^2(H^1\psi_n^1 + H^0\psi_n^2) = E_0\psi_n^0 + \lambda(E_n^1\psi_n^0 + E_n^0\psi_n^1) + \lambda^2(E_n^0\psi_n^2 + E_n^1\psi_1^1 + E_n^2\psi_n^0)$$

We now claim that the terms have to separate because they are linearly independent. We have the λ^0 terms:

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

The λ^1 terms:

$$H^1\psi_n^0 + H^0\psi^1 = E_n^1\psi_n^0 + E_n^0\psi_n^1$$

And we will have the λ^2 terms as well, I just don't want to write them out. The way we pull information out of these equations is that we use the fact that ψ_n^0 are orthonormal and complete. Recall that orthonormality means that

$$\langle\psi_m^0|\psi_n^0\rangle = \delta_{mn}$$

and completeness tells us that

$$\sum_i |\psi_i^0\rangle \langle\psi_i^0| = I$$

Suppose we take the second equation, the one from the λ terms, and we take the inner product from the left using $\langle\psi_n^0|$:

$$\langle\psi_n^0| (H^1 |\psi_n^0\rangle + H^0 |\psi^1\rangle) = \langle\psi_n^0| (E_n^1 |\psi_n^0\rangle + E_n^0 |\psi_n^1\rangle)$$

$$\langle\psi_n^0|H^1|\psi_n^0\rangle + \langle\psi_n^0|H^0|\psi_n^1\rangle = \langle\psi_n^0|E_n^1|\psi_n^0\rangle + \langle\psi_n^0|E_n^0|\psi_n^1\rangle$$

This may seem bad, but if we look at the second term on the left side, we can apply H^0 to the state to $\langle\psi_n^0|$, we get $\langle\psi_n^0| E_n^0 |\psi_n^1\rangle$:

$$\langle\psi_n^0|H^1|\psi_n^0\rangle + E_n^0 \langle\psi_n^0|\psi_n^1\rangle = E_n^1 \langle\psi_n^0|\psi_n^0\rangle + E_n^0 \langle\psi_n^0|\psi_n^1\rangle$$

And we see that two terms cancel:

$$\langle\psi_n^0|H^1|\psi_n^0\rangle = E_n^1$$

We see that we have an expression for a matrix element of the perturbing Hamiltonian. This gives that the first order correction to the energy is going to be a matrix element of our Hamiltonian, and is true for all n.

We could show that the first order correction to the wavefunction is given by

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

Note that this does not work for states that has two states with the same energy, as the correction to the wavefunction will diverge. This is first-order, non-degenerate perturbation theory.

4.1 Degenerate Perturbation Theory

Suppose we have two states, ψ_a^0 and ψ_b^0, which have the same energy E_n^0. We now orthogonalize them using the Gram-Schmidt process to set it up suhc that $\langle \psi_a^0 | \psi_b^0 \rangle = 0$. Now we again plug into the same perturbation theory equation we found, except we plug in linear combinations of ψ_a^0 and ψ_b^0 instead:

$$\psi_n^0 = \alpha \psi_a^0 + \beta \psi_b^0$$

We find that (usually), H^1 "breaks" the degeneracy. Taking the inner product from the left with ψ_a^0 gets us:

$$\alpha \langle \psi_a^0 | H^1 | \psi_a^0 \rangle + \beta \langle \psi_a^0 | H^1 | \psi_b^0 \rangle = \alpha E^1$$

We call this first term W_{aa}, and the second term W_{ab}:

$$\alpha W_{aa} + \beta W_{bb} = \alpha E^1$$

And if we instead take the inner product from the left with ψ_b^0:

$$\alpha W_{ba} + \beta W_{bb} = \beta E^1$$

We can put these two together:

$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

This is an eigenvalue problem, and can be solved for E^1, as well as α and β. We will get raising and lowering operators:

$$E_\pm^1 = \frac{1}{2} \left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb}) + 4|W_{ab}|^2} \right]$$

And we can compute the ratio between β and α:

$$\left(\frac{E_\pm^1 - W_{aa}}{W_{ab}} \right) \alpha = \beta_\pm$$

For higher degeneracy, we have a larger matrix, where we introduce new states labelled by c, d, etc. This matrix is known as $\hat{W}$. We have that $\det(\hat{W} - E^1 I) = 0$. If we have this, we can find all the energies, and we can find all the coefficients if we wanted.

4.1.1 Relativistic Corrections to the Hydrogen Atom

When we looked at the Bohr/Schrodinger model of the Hydrogen atom, and compared it against the experimental spectra, we found that we saw "splitting", experimental spectra had multiple lines where the theoretical spectra had only 1.

When we write out the energy of the hydrogen atom:

$$E_{nlm} = -\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\frac{1}{n^2}$$

We can rewrite this as

$$E_n = -\frac{m_e c^2}{2}\left(\frac{e^2}{4\pi\hbar\varepsilon_0 c}\right)^2\frac{1}{n^2}$$

Now we note that

$$E_1 = 13.6eV = \frac{m_e c^2}{2}\left[\frac{e^2}{4\pi\varepsilon_0\hbar c}\right]^2$$

Now we note that $m_e c^2 = 511$ keV, which tells us that the squared term is small. The inside of that term is given a name, the fine-structure constant:

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

We will see that the spectral splitting depends on this constant. We can get rid of the c via the relationship

$$c = \sqrt{\frac{1}{\varepsilon_0\mu_0}}$$

Giving that

$$\alpha = \frac{e^2}{4\pi\hbar}\sqrt{\frac{\mu_0}{\varepsilon_0}}$$

We note that this square root term is the impedance of free space, $Z_0 = 376.73\Omega$. From this, we know that $\frac{4\pi\hbar}{e^2} = 51625.6\Omega$, which is sometimes known as the quantum resistance.

If we look at the Bohr model and compute the current of the electron:

$$I = \frac{e}{T} \cong \omega e = (\hbar\omega)\frac{e}{\hbar} = E_1\frac{e}{\hbar}$$

We can compute the voltage, which is energy per unit charge:

$$V = \frac{E_1}{e}$$

Now using Ohm's law:

$$\frac{V}{I} = \frac{\hbar}{e^2}$$

We've dropped a factor of π in the frequency, but we see that we have the same ratio that we had in α.

We have that $\frac{E_1}{m_e c^2} \propto \alpha^2$, and we have corrections to this. We have that the electron has kinetic energy, which gives small relativistic corrections, of order α^2. We then have the interaction between the spin and the orbit give a correction of order α^2. Together, these account for the "fine structure".

We have spent our time in quantum mechanics by saying that the kinetic energy is given by

$$T = \frac{p^2}{2m} \quad p = \frac{h}{i}\nabla$$

We have the $\hat{T}$ operator:

$$\hat{T} = -\frac{\hbar^2}{2m}\nabla^2$$

This is the classical limit. We need something different to account for relativity. From relativity, we have that

$$E = \frac{mc^2}{\sqrt{1 - \left(\frac{v}{2}\right)^2}}$$

The rest energy ($v = 0$), is given by mc^2. Thus the kinetic energy will be the total energy minus the rest energy:

$$T_{\text{rel}} = \frac{mc^2}{\sqrt{1 - \left(\frac{v}{2}\right)^2}} - mc^2$$

Note that if v is small, we can do a Taylor series expansion and we will find the classical limit, $\frac{1}{2}mv^2$.

Now we need to express this in terms of p, but p is not mv in relativity:

$$p = \frac{mv}{\sqrt{1 - \left(\frac{v}{c}\right)^2}}$$

In special relativity, where $V = 0$, we have that

$$E^2 = p^2c^2 + m^2c^4$$

To get the relativistic kinetic energy, we have to find

$$T = E(p) - E(p = 0) = \sqrt{p^2c^2 + m^2c^4} - mc^2$$

Now we note that p^2c^2 is small if $v \ll c$. We can rewrite the kinetic energy:

$$T = mc^2\sqrt{1 + \frac{p^2}{m^2c^2}} - mc^2$$

Now we can do a Taylor series expansion:

$$T = mc^2\left[1 + \left(\frac{p}{mc}\right)^2\frac{1}{2} - \frac{1}{8}\frac{p^4}{m^4c^4} + \dots\right] - mc^2$$

We see that we are left with

$$T = \frac{p^2}{2m} - \frac{\left(\frac{p^2}{2m}\right)^2}{2mc^2}$$

Thus we have that

$$\hat{H} = \frac{\hat{p}^2}{2m} + V - \frac{\left(\frac{\hat{p}^2}{2m}\right)^2}{2mc^2}$$

We call the first two terms H, and the last term H'.

Now we can compute the first order corrections to the energy:

$$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle = \left\langle \psi_n^0 \middle| \left(\frac{p^2}{2m}\right)^2 \middle| \psi_n^0 \right\rangle \left(-\frac{1}{2mc^2}\right)$$

$$= \left\langle \frac{p^2}{2m}\psi_n^0 \middle| \frac{p^2}{2m}\psi_n^0 \right\rangle \left(-\frac{1}{2mc^2}\right)$$

Computing the value of $\frac{p^2}{2m}\psi_n^0$ for the infinite square well:

$$\frac{p^2}{2m}\psi_n^0 = -\frac{\hbar^2}{2m}\frac{d^2}{dx}\left[\sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}\right]$$

And we can do this out and we find that we have

$$E_n^1 = \left(-\frac{1}{2mc^2}\right)(E_n^0)^2$$

Looking at the unperturbed state, we have that

$$\frac{p^2}{2m} = (E_n^0 - V)$$

This turns the relativistic correction that we just computed into:

$$E_n^1 = \left\langle (E_n^0 - V)\psi_n^0 \middle| (E_n^0 - V)\psi_n^0 \right\rangle \left(-\frac{1}{2mc^2}\right)$$

$$= \left\langle \psi_n^0 \middle| (E_n^0 - V)^2 \middle| \psi_n^0 \right\rangle \left(\frac{-1}{2mc^2}\right) = \left\langle \psi_n^0 \middle| (E_n^0)^2 - 2E_n^0 V + V^2 \middle| \psi_n^0 \right\rangle \left(-\frac{1}{2mc^2}\right)$$

$$= \left[(E_n^0)^2 - 2E_0 \left\langle \psi_n^0 \middle| V \middle| \psi_n^0 \right\rangle + \left\langle \psi_n^0 \middle| V^2 \middle| \psi_n^0 \right\rangle\right] \left(-\frac{1}{2mc^2}\right)$$

Now we can recall that $V = \frac{-c^2}{4\pi\varepsilon_0 r}$, and we have two awful inner products, with the V, which boil down to $\left\langle \frac{1}{r} \right\rangle$ and $\left\langle \frac{1}{r^2} \right\rangle$:

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a} \qquad a = \frac{4\pi\varepsilon_0\hbar^2}{me^2}$$

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{\left(l + \frac{1}{2}\right) n^3 a^2}$$

We can write out the correction as

$$\frac{E_n^1}{|E_n^0|} = -\frac{\alpha^2}{4}\left[\frac{4}{n(l+\frac{1}{2})} - \frac{3}{n^2}\right]$$

Unfortunately, this does not agree with experiment. The reason is that this is incomplete, there is another term of order α^2 that needs to be included. This term is the spin-orbit coupling. The idea is that we have a proton with an electron orbiting around it. If we momentarily go into the frame of the electron, we have the proton orbiting around the electron. Since we have a moving charge, we produce a magnetic field. The electron has a magnetic moment with interacts with the magnetic field, $-\mu \cdot \mathbf{B}$. The spin creates the μ and the orbit generates the magnetic field $\mathbf{B}$.

Note that we have a warning alarm blaring here, we've switched to a non-inertial reference frame. Newton's laws state that $\sum \mathbf{F} = m\mathbf{a}$. We can split $\mathbf{a}$ into the centripetal acceleration and another term, where the centripetal acceleration is

$$\mathbf{a}_c = -\frac{v^2}{r}\mathbf{r} = -r\omega^2\hat{r}$$

This gives us that

$$\sum \mathbf{F} = m(\mathbf{a}_c + \tilde{\mathbf{a}}) = -mr\omega^2\hat{r} + m\tilde{\mathbf{a}}$$

We can rewrite this:

$$\sum \mathbf{F} + m\omega^2 r\hat{r} = m\tilde{\mathbf{a}}$$

This term on the left side that we've added is the inertial force, the centripetal force. Thus to work in the rotating frame, we need an extra term to account for it. We can get the potential for this force by just integrating it. For now though, we just ignore it (going along with the book).

The book just looks at

$$H = -\mu \cdot \mathbf{B} = -(\mu_x B_x + \mu_y B_y + \mu_z B_z)$$

So now we need to find what $\mathbf{B}$ is. We use the dreaded Biot-Savart Law:

$$d\mathbf{B} = \frac{\mu_0}{4\pi}\frac{I\, d\mathbf{l} \times \hat{r}}{|\mathbf{r}|^2}$$

We also have:

$$M_e = -\frac{e}{m}\mathbf{S}$$

Where $\mathbf{S}$ is the spin angular moment. If we put this all together with the Hamiltonian:

$$H = -\mu \times \mathbf{B} = \frac{e^2}{4\pi\varepsilon_0}\frac{1}{2}\frac{1}{m^2c^2r^3}\mathbf{S}\cdot\mathbf{L}$$

Where we have added a factor of $\frac{1}{2}$ because we are working in the rotating reference frame. Since we have the spin operator and the angular momentum operator, this is known as the spin-orbit interaction.

It turns out that there is an operator $\hat{J}$, which is the total angular momentum operator:

$$\hat{J} = \hat{L} + \hat{S}$$

We use this because $\hat{S}$ and $\hat{L}$ don't commute with the Hamiltonian. We use $\hat{J}^2 = (\hat{S} + \hat{L})^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{L}\hat{S}$. This turns the Hamiltonian into

$$H = \frac{e^2}{8\pi\varepsilon_0}\frac{1}{m^2c^2r^3}\frac{1}{2}[\hat{J}^2 - \hat{L}^2 - \hat{S}^2]$$

4.2 Summary of Perturbation Theory

Let's do a summary. We have non-degenerate perturbation theory:

$$H = H^0 + H^1$$

$$E_n = E_n^0 + E_n^1 + E_n^2 + \dots$$

Where the exponents are indices. We find that the first order corrections to the energy are:

$$E_n^1 = \langle \psi_n^0 | H^1 | \psi_n^0 \rangle$$

And the second order corrections are given by

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

Note that if we had H^0 in there instead, we would have 0 as the second order corrections. We then have the first order correction to the wavefunction:

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

Note that these formulas come from orthonormality and completeness, we are expanding out the corrections in the original wavefunction basis.

For degenerate perturbation theory, we note that we haev an issue when $E_m = E_n$, we have states that are degenerate in energy. We state that there are orthogonal states:

$$\psi^0 = \alpha \psi_a^0 + \beta \psi_b^0 + \gamma \psi_c^0 + \dots$$

These states are states of the unperturbed Hamiltonian, with the same energy, E^0. We then get

$$W \begin{pmatrix} \alpha \\ \beta \\ \gamma \\ \delta \\ \vdots \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \\ \gamma \\ \delta \\ \vdots \end{pmatrix}$$

Where $W_{ab} = \langle \psi_a^0 | H^1 | \psi_b^0 \rangle$. If we then set $\det(W - E^1 I) = 0$, we can solve for the energies.

5 The Variational Principle

The variational principle starts with a trial wavefunction. We then compute the corresponding energy, and then we shift the "width" of the trial wavefunction to find the minimum energy, which will be $\geq E_{\text{ground}}$.

We have some H, which is unsolved. However, it will have states $|\psi_n\rangle$ with E_n, but we have no clue what they are. By orthonormality and completeness, we can expand any state using those:

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

Where $H|\psi_n\rangle = E_n |\psi_n\rangle$, as expected from QM. Let us take an arbitrary state, and compute the magnitude:

$$\langle \psi | \psi \rangle = \sum_{n'} c_{n'}^* \langle \psi_{n'} | \sum_n c_n |n\rangle = \sum_{n,n'} c_{n'}^* c_n \langle n' | n \rangle = \sum_n |c_n^2| = 1$$

Let us compute the expectation value of H for a state $|\psi\rangle$:

$$\langle\psi|H|\psi\rangle = \sum_n c_n^* \langle\psi_n| H \sum_m c_m |\psi_m\rangle = \sum |c_n|^2 E_n$$

The ground state is the state with the lowest energy:

$$E_0 \leq E_1, E_2, E_3, \ldots$$

Thus we know that

$$\langle\psi|H|\psi\rangle = \sum_n |c_n|^2 E_n \geq \sum_n |c_n|^2 E_0 = E_0$$

This tells us that for any Hamiltonian, and for any state $\langle\psi|H|\psi\rangle \geq E_0$.

Suppose we have an infinite square well, centered at the origin, ranging from $-\frac{a}{2}$ to $\frac{a}{2}$. We submit that anything that is smooth and is 0 at the edges, and has a little bit of squiggle is a good enough guess to start. We want to find some inverted quadratic, which is something like

$$\psi_{\text{guess}} = c\left(x - \frac{a}{2}\right)\left(x + \frac{a}{2}\right)$$

We then need to normalize this, which will determine c:

$$|\psi_{\text{guess}}|^2 = |c|^2 \left(x^2 - \frac{a^2}{4}\right)^2 = |c|^2 \left(x^4 - 2x^2\frac{a^2}{4} + \frac{a^4}{16}\right)$$

Now normalizing:

$$\int_{-\frac{a}{2}}^{\frac{a}{2}} |\psi_{\text{guess}}|^2 \, dx = 1 \to \frac{|c|^2 a^5}{30} = 1$$

This tells us that $c = \left(\frac{30}{a^5}\right)^{\frac{1}{2}}$. We now want to compute $\langle\psi|H|\psi\rangle$:

$$\langle\psi|H|\psi\rangle = \langle\psi| \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\left(cx^2 - c\left(\frac{a}{2}\right)^2\right)\right] = \langle\psi| -\frac{\hbar^2}{2m} 2c = \langle\psi| \left[-\frac{2\hbar^2 c}{2m}\right] = \int_{-\frac{a}{2}}^{\frac{a}{2}} c^* x^2 - x^* \frac{a^2}{4}\left(-\frac{\hbar^2}{2m}c\right) dx$$

We find that

$$\langle\psi|H|\psi\rangle = \frac{1}{3}|c|^2 \frac{\hbar^2 a^3}{2m} = \frac{10\hbar^2}{2ma^2}$$

We know that the energy of the ground state is actually $\frac{\hbar^2}{2m}\frac{\pi^2}{a^2}$. This is about a 6% difference between the actual ground state and the guess wavefunction. Note that in most cases where we use this method, we won't know the actual ground state energy.

This method is called the variational principle, but we didn't vary anything! Let us do an example where we do so. Take the harmonic oscillator potential, which is difficult to solve. Suppose we try the same wavefunction as in the previous example, noting that there is no clear choice of a. This time, we do the analogous calculation to find $\langle\psi|H|\psi\rangle$, and then we vary a to minimize this value.

We still have that

$$\int_{-\frac{a}{2}}^{\frac{a}{2}} \psi^* \psi \, dx = 1$$

Which still obtains $|c|^2 a^5 = 30$. We can then set up the integral for $\langle\psi|H|\psi\rangle$:

$$\int_{-\frac{a}{2}}^{\frac{a}{2}} \psi^* \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2\right)\psi \, dx$$

We can first compute the action of the Hamiltonian on ψ:

$$H\psi = \left(-\frac{\hbar^2}{m} + \frac{1}{2}m\omega^2 x^4 - \frac{1}{8}m\omega^2 a^2 x^2\right) c$$

And then tacking on ψ^* to this:

$$\psi^* H\psi = |c|^2 \left[\frac{1}{2}m\omega^2 x^6 - \frac{1}{4}m\omega^2 a^2 x^4 + \left(\frac{1}{32}m\omega^2 a^4 - \frac{\hbar^2}{m}\right) x^2 + \frac{\hbar^2}{4m}a^2\right]$$

We then have to integrate this from $-\frac{a}{2}$ to $\frac{a}{2}$:

$$\langle H\rangle = 60\left[a^2 m\omega^2 \frac{1}{3360} + \frac{\hbar^2}{m}\frac{1}{a^2}\frac{1}{12}\right]$$

If we take the derivative with respect to a, and setting it equal to 0 will give us the minima and maxima of this expression. We can then take the "best" value of a and find $\langle H\rangle_{\min}$. We will find that $a_{\min} = \frac{3360}{12}\sqrt{\frac{\hbar^2}{m\omega}}$, and $\langle H\rangle_{\min} = \sqrt{\frac{5}{14}}\hbar\omega = 0.598\hbar\omega$. This is off by about 20%.

5.1 Ground State of Helium with Variational Principle

We want to use the variational principle to find the ground state of helium. The Hamiltonian is given by

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

Where we have the kinetic energy of both particles, and then the potential energies of the electrons and the proton, and then the potential between the two.

If we ignore the electron-electron interaction, then we have that

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)$$

For hydrogen, we have that

$$\psi_{100} = \sqrt{\frac{1}{\pi a^3}}e^{-r/a} \quad E = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2$$

Where we have that $n = 1$, so that gets rid of the $\frac{1}{n^2}$, and $a = \frac{4\pi\varepsilon_0\hbar^2}{me^2}$. We have to modify this for Helium, because $e^2 \to 2e^2$. If we write the Hydrogen wavefunction out but change the e^2 to $2e^2$:

$$\psi_{100}(\mathbf{r}_1) = \sqrt{\frac{2^3}{\pi a^3}}e^{-2r_1/a}$$

and similarly for $\psi_{100}(\mathbf{r}_2)$. Putting the two functions back together:

$$\psi_{100}(\mathbf{r}_1\mathbf{r}_2) = \frac{8}{\pi a^3}e^{-2(\mathbf{r}_1+\mathbf{r}_2)/a}$$

We want to use this as our trial wavefunction. We can then compute the inner product $\langle\psi_{100}|H|\psi_{100}\rangle$:

$$E_0 \leq \langle 100|T + V(e_1, p) + V(e_2, p)|100\rangle + \langle 100|V(e, e)|100\rangle$$

$$\leq -8E_{ion}^{H} + \frac{e^2}{4\pi\varepsilon_0}\left(\frac{8}{\pi a^3}\right)^2 \int_{\mathbf{r}_1}\int_{\mathbf{r}_2} e^{-4(r_1+r_2)/a}\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\,d^3r_1 d^3r_2$$

To do this, we first fix $\mathbf{r}_1$, and we can then write $|\mathbf{r}_1-\mathbf{r}_2| = \sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}$, using the law of cosines. We can then change the r_2 integral to spherical:

$$\langle V_{ee}\rangle = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{8}{\pi a^3}\right)^2 \int_{\mathbf{r}_1}\left[\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\frac{e^{-4r_2/a}r_2^2\sin\theta_2\,dr_2 d\theta_2 d\phi_2}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}}\right] e^{-4r_1/a}\,d^3\mathbf{r}_1$$

We see that the ϕ_2 integral is easy, it only shows up once:

$$= 2\pi\int_0^{\infty} e^{-4r_2/a}r_2^2\int_0^{\pi}\frac{\sin\theta_2 d\theta_2}{\sqrt{r_1^2+r-2^2-2r_1r_2\cos\theta_2}}\,dr_2$$

Through magic, we find that

$$\langle V_{ee}\rangle = \left(\frac{e^2}{4\pi\varepsilon_0 a}\right)\frac{5}{4} = \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\frac{5m}{4\hbar^2}$$

We find that $E_0^{He} \leq -74.8$ eV, and experiment shows that the energy is -78.975 eV.

We now account for the fact that one electron partially screens the nucleus from the other electron. Instead of saying $e^2 \to 2e^2$, we instead say $e\cdot e \to Z_{\text{eff}}e\cdot e$, where we expect that $Z_{\text{eff}} < 2$. This is the parameter that we want to vary.

We find that the Z_{eff} that gives the minimum in the energy is $\frac{27}{16}$, and the ground state energy is ≤ -77.5eV, which is closer to the experimental value.

6 WKB/KWB/BWK/JWKB/LG Method

The main idea of this approximation is that if V is constant, and $E > V$, ψ will be plane waves, Ae^{ikx}, where $k = \sqrt{\frac{2m(E-V)}{\hbar^2}}$. If V varies slowly, maybe we can get away with

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

What we want is for the wavelength to vary slowly, so everything is fine unless $E-V$ is approaching 0. Therefore, we have issues near the classical turning points of the potential.

We define $k(x) = \sqrt{\frac{2m}{\hbar^2}(E-V(x))}$, for $E > V(x)$. We then define the momentum, $p(x) = \hbar k(x) = \sqrt{2m(E-V(x))}$. Our Schrodinger equation then becomes

$$\frac{d^2\psi(x)}{dx^2} = -\frac{(p(x))^2}{\hbar^2}\psi(x)$$

All we have done is rewrite this using our definitions, just to remove constants that we have to carry around. Now let us look for a solution of the form $A(x)e^{i\phi(x)}$. This is a general form of a complex function, it has a phase and an amplitude.

We have that the first derivative of our function is

$$\frac{d\psi}{dx} = \frac{dA(x)}{dx}e^{i\phi(x)} + iA(x)\frac{d\phi}{dx}e^{i\phi(x)}$$

Now we take the derivative of this, and insert it into the Schrodinger equation:

$$\frac{d^2\psi}{dx^2} = \left[\frac{d^2A}{dx^2} + 2i\frac{dA}{dx}\frac{d\phi}{dx} - A\left(\frac{d\phi}{dx}\right)^2 + iA\frac{d^2\phi}{dx^2}\right]e^{i\phi(x)} = -\frac{p^2(x)}{\hbar^2}A(x)e^{i\phi(x)}$$

This is actually 2 equations, since we have the left side being complex and the right side being real. Thus we can write out two equations:

$$\frac{d^2A}{dx^2} = A\left[\left(\frac{d\phi}{dx}\right)^2 - \frac{p^2(x)}{\hbar^2}\right]$$

$$i\left[2\frac{dA}{dx}\frac{d\phi}{dx} + A\frac{d^2\phi}{dx^2}\right] = 0$$

We can rewrite the second equation, (take derivative and divide by A):

$$\frac{d^2A}{dx^2} = A\left[\left(\frac{d\phi}{dx}\right)^2 - \frac{p^2(x)}{\hbar^2}\right]$$

$$\frac{d}{dx}\left[A^2\frac{d\phi}{dx}\right] = 0$$

If we now integrate the second equation, we have that $A^2\frac{d\phi}{dx} = D^2$, giving us

$$A = \frac{D}{\sqrt{\frac{d\phi}{dx}}}$$

Now we have that $A(x)$ and $\phi(x)$ are related by some constant D. Looking at the first equation, (after some rewriting)

$$\frac{1}{A}\frac{d^2A}{d^2} = \left(\frac{d\phi}{dx}\right)^2 - \frac{p^2}{\hbar^2}$$

Now we claim that if $V(x)$ varies slowly, the term on the left is close to 0, and thus we can drop the term. We can check this later, after finding our solution.

We find that

$$\psi_\pm = \frac{C_\pm}{\sqrt{p(x)}}e^{\pm i\int^x p(x')\,dx}$$

For regions where $E > V$ (oscillatory behavior). For regions where $E < V$:

$$\psi = \frac{D_\pm}{\sqrt{|p(x)|}}e^{\pm\frac{1}{\hbar}\int^x |p(x')|\,dx}$$

We see that we have exponential decay. Now we need to find the solution in the "danger" regions, so we can match the wavefunctions and their derivatives at the edges of the regions to get a full solution. Suppose we zoom in on the section of the potential close to the danger point. If we zoom in close enough to the turning point, the potential is linear in x. If we move the origin to the turning point, we have that the potential at some x close to 0 is $V(x) = V(0) + V'(0)x$, where $V'(0) = \frac{dV(x)}{dx}|_0$. We can insert this into the Schrodinger equation:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \big(E + V'(0)x\big)\,\psi = E\psi$$

Which gets us

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}V'(0)x\psi$$

We note that $\frac{2m}{\hbar^2}V'(0)$ has units of length^{-3}. We define a quantity α:

$$\alpha = \left[\frac{2m}{\hbar^2}V'(0)\right]^{1/3}$$

This turns our equation into

$$\frac{d^2\psi}{dx^2} = \alpha^3 x\psi$$

Which we can change of variables into

$$\frac{d^2\psi}{d(\alpha x)^2} = \alpha x\psi$$

If we let $z = \alpha x$, we have the equation

$$\frac{d^2\psi}{dz^2} = z\psi$$

This was solved by the astronomer Airy, and are known as Airy functions, which have special properties.

$$\psi(z) = a\,\mathrm{Ai}(z) + b\,\mathrm{Bi}(z)$$

We can look at the asymptotic forms of Ai on both ends, where we see that from the left, we have

$$\frac{1}{(-z)^{1/4}}\sin\left(\frac{2}{3}(-z)^{3/2} + \frac{\pi}{4}\right)$$

and from the right, we have

$$\frac{1}{z^{1/4}}e^{-\frac{2}{3}z^{3/2}}$$

For Bi, instead of a sin, we have a cos, and instead of a decaying exponential we have exponential growth.

They also have the property that

$$\langle Ai(z)|Ai(z')\rangle = \delta(z - z') \quad \langle Ai(z)|Bi(z')\rangle = 0$$

We can then use wavefunction matching, and we can write down the wavefunctions:

$$\psi(x) = \frac{2D}{\sqrt{p(x)}}\sin\left(\frac{1}{\hbar}\int_x^{x_2} p(x')\,dx' + \frac{\pi}{4}\right) \quad x < x_2$$

$$\psi(x) = \frac{D}{\sqrt{p(x)}}\exp\left(-\frac{1}{\hbar}\int_{x_2}^{x} |p(x')|\,dx'\right) \quad x > x_2$$

Where we have defined the wavefunctions for the right turning point. We can do the same thing for the right turning point, at x_1:

$$\psi(x) = \frac{2D}{\sqrt{p(x)}}\sin\left(\frac{1}{\hbar}\int_{x_1}^{x} p(x')\,dx' + \frac{\pi}{4}\right) \quad x > x_1$$

We now note that the inner well wavefunctions must be equal to each other:

$$\psi(x) = \frac{2D'}{\sqrt{p(x)}} \sin\left(\frac{1}{\hbar}\int_{x_1}^{x} p(x')\,dx' + \frac{\pi}{4}\right) \quad x > x_1$$

$$\psi(x) = \frac{2D}{\sqrt{p(x)}} \sin\left(\frac{1}{\hbar}\int_{x}^{x_2} p(x')\,dx' + \frac{\pi}{4}\right) \quad x < x_2$$

Because sin is odd, we can flip the sign in the first case:

$$\psi(x) = \frac{2D'}{\sqrt{p(x)}} \sin\left(-\frac{1}{\hbar}\int_{x_1}^{x} p(x')\,dx' - \frac{\pi}{4}\right) \quad x > x_1$$

We now have that the arguments to the sines are the same, up to a mod of $n\pi$:

$$\frac{1}{\hbar}\int_{x}^{x_2} p(x')\,dx' + \frac{\pi}{4} = -\frac{1}{\hbar}\int_{x_1}^{x} p(x')\,dx' - \frac{\pi}{4} + n\pi$$

Now noting that bringing one integral to the other side gives an integral over the entire classical region:

$$\frac{1}{\hbar}\int_{x_1}^{x_2} p(x')\,dx' + \frac{\pi}{2} = n\pi$$

$$\boxed{\int_{x_1}^{x_2} p(x')\,dx' = \left(n - \frac{1}{2}\right)\pi\hbar}$$

Now we recall that $p = \pm\sqrt{2m(E-V)}$, and we note that we have an implicit equation for the energy eigenvalues. This is the Bohr-Sommerfeld Quantization condition. If we insert the harmonic oscillator potential, $V = \frac{1}{2}m\omega^2x^2$, we get the right answer.

7 Dynamics

Long ago, all quantum mechanics textbooks stated that we can separate the wavefunction into a time dependent part and a position dependent part:

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})e^{-iEt/\hbar}$$

And a general $\Psi(\mathbf{r}, t)$ is given by

$$\Psi(\mathbf{r}, t) = \sum_n c_n\psi_n(\mathbf{r})e^{-E_nt/\hbar}$$

Via orthonormality and completeness.

Suppose we have a Hydrogen atom sitting in the $n = 3$ state in some potential. Our theory states that it will remain like this forever, since the $n = 3$ state is an eigenstate ($\psi^*\psi$ is time-independent). However, we don't see this in reality, so what's missing?

We are missing the fact that real atoms decay. Suppose $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\mathbf{r}|} + \hat{z}E_0\cos(\omega t)$, where we have the Hydrogen atom, as well as some laser being shone at the atom, polarized in the $\hat{z}$ direction. Now we have a time-dependent potential, so how do we deal with this?

Dynamics is when the state is changing in the Hilbert space, instead of the usual $P_a = |c_a|^2$, we have that P_a is some function of t. To make this change, we move from a time-independent potential to a time-dependent potential.

Suppose we have a two-state system, such as spin, or a qubit, or anything that acts like a two state system.

We choose a Hamiltonian $H = H^0 + H'(t)$, where H^0 is static, and we note that H' does not need to be small. We have ψ_a and ψ_b, which form a basis for H^0:

$$H^0\psi_a = E_a\psi_a \quad H^0\psi_b = ES_b\psi_b$$

Now we can go back to the full time dependent equation, and find the states:

$$(H^0 + H')\Psi(t) = i\hbar\frac{\partial}{\partial t}\Psi(t)$$

We will look for solutions of the form $\Psi(t) = c_a(t)e^{-iE_at/\hbar}\psi_a + c_b(t)e^{-iE_bt/\hbar}\psi_b$. Inserting this into the Hamiltonian and then expanding out and cancelling terms:

$$H'\left[c_a(t)\psi_a e^{-iE_at/\hbar} + c_b(t)\psi_b e^{-iE_bt/\hbar}\right] = i\hbar\left[\dot{c}_a\psi_A e^{-iE_at/\hbar} + \dot{c}_b\psi_b e^{-iE_bt/\hbar}\right]$$

This is the basic equation for time-dependent perturbation theory. We then do the usual trick, replace the basis states with kets, and then operate on both sides with a $\langle\psi_a|$, we will have matrix elements as well as cancellation of some terms:

$$c_a(t)e^{-iE_at/\hbar}\langle\psi_a|H'|\psi_a\rangle + c_b(t)e^{-iE_bt/\hbar}\langle\psi_a|H'|\psi_b\rangle = i\hbar\dot{c}_a e^{-iE_at/\hbar}$$

$$c_a e^{-iE_at/\hbar}H'_{aa} + c_b e^{-iE_bt/\hbar}H'_{ab} = i\hbar\dot{c}_a e^{-iE_at/\hbar}$$

Now suppose we had taken the inner product with $\langle\psi_b|$ instead, and we would find a similar equation, just with interchange of as and bs:

$$c_b e^{-iE_bt/\hbar}H'_{bb} + c_a e^{-iE_at/\hbar}H'_{ba} = i\hbar\dot{c}_b e^{-iE_bt/\hbar}$$

Note that these two equations are exact, we haven't made any approximations. We can now solve these equations for the coefficient derivatives:

$$\dot{c}_a(t) = -\frac{i}{\hbar}H'_{ab}(t)e^{-i\omega_0 t}c_b(t)$$

$$\dot{c}_b(t) = -\frac{i}{\hbar}H'_{ba}(t)e^{i\omega_0 t}c_a(t)$$

Where $\omega_0 = \frac{E_b - E_a}{\hbar}$. To solve these, we can use initial conditions, such as that it starts in state a, which tells us that $c_a(0) = 1$ and $c_b(0) = 0$. We then claim that the 0th iteration solution is that $c_a^0(t) = 1$ and $c_b^0(t) = 0$, and then plug these into the equations to get the first iteration solutions:

$$\dot{c}_a^1 = -\frac{i}{\hbar}H'_{ab}e^{-i\omega_0 t}c_b^0 \to c_a^1 = 1$$

$$\dot{c}_b^1 = -\frac{i}{\hbar}H'_{ba}e^{i\omega_0 t}c_a^0 \to c_b^1 = \frac{-i}{\hbar}\int_0^t H'_{ba}(t')e^{i\omega_0 t'}\,dt'$$

Note that we have to renormalize the solutions that we find. The general scheme, using iteration indices:

$$\dot{c}_a^{n+1} = -\frac{i}{\hbar}H_{ab}(t)e^{-i\omega_0 t}c_b^n(t)$$

$$\dot{c}_b^{n+1}(t) = -\frac{i}{\hbar} H'_{ba}(t) e^{i\omega_0 t} c_a^n(t)$$

This is the heart of time-dependent perturbation theory. We can write out the expression for c_b:

$$c_b(t) = -\frac{i}{\hbar} \int_0^t e^{i(E_b - E_a)t'/\hbar} H'_{ba}(t')\, dt'$$

If we do this out, we have

$$e^{-iE_b t/\hbar} c_b(t) = -\frac{i}{\hbar} \int_0^t \left[\int (e^{-iE_b(t-t')/\hbar} \psi_b^*(q)) H'(t') (e^{-iE_a t'/\hbar} \psi_a(q))\, dq \right] dt'$$

We see that we accumulate the influence of the perturbation in the past in the matrix element.

Suppose that we have a time dependent Hamiltonian, with $H' = V_{ba} \cos(\omega t)$. This turns the integral into

$$c_b^{(1)}(t) = -\frac{i}{\hbar} \int_0^t V_{ba} \cos(\omega t') e^{i\omega_0 t'}\, dt'$$

This is solvable, by converting the cos to exponentials:

$$\cos(\omega t') = \frac{e^{i\omega t'} + e^{-i\omega t'}}{2}$$

This turns the integral into

$$c_b^{(1)}(t) = -\frac{iV_{ba}}{2\hbar} \int_0^t e^{i\omega t' + i\omega_0 t'} + e^{-i\omega t' + i\omega_0 t'}\, dt = -\frac{iV_b a}{2\hbar} \left[\int_0^t e^{it'(\omega + \omega_0)}\, dt + \int_0^t e^{it'(\omega_0 - \omega)}\, dt \right]$$

$$= -\frac{V_{ba}}{2\hbar} \left[\frac{e^{i(\omega+\omega_0)t'}}{\omega_0 + \omega} + \frac{e^{i(\omega_0-\omega)t'}}{\omega_0 - \omega} \right]_0^t = -\frac{V_{ba}}{2\hbar} \left[\frac{e^{i(\omega_0+\omega)t'} - 1}{\omega_0 + \omega} + \frac{e^{i(\omega_0-\omega)t'} - 1}{\omega_0 - \omega} \right]$$

If we have that ω is close to ω_0, then the first term will have a denominator of $2\omega_0$, while $\omega_0 - \omega$ will be small. Thus we can make an approximation, which is to drop the first term.

We can then rewrite the term that we have remaining (using the nice trick of factoring out a $e^{i\omega t/2}$, which will make the inside a factor of the sin), and then get the magnitude to find the probability:

$$P_b^{(1)}(t) = |c_b^{(1)}(t)|^2 = \frac{|V_{ba}|^2}{\hbar^2} \left(\frac{\sin\left(\frac{\omega_0 - \omega}{2} t\right)}{\omega_0 - \omega} \right)$$

This is the probability that, starting in the ground state a, the you are in the upper state b. The oscillations in the probability are known as Rabi oscillations.

Let us go back a few steps, and write down the exact formulas:

$$\dot{c}_a^1 = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b^0$$

$$\dot{c}_b^1 = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a^0$$

If we now insert that $H'_{ab} = V_{ba} \cos \omega t$, and $H'_{ba} = V_{ba} \cos \omega t$, we have exact equations.

$$\dot{c}_a = -\frac{iV_{ab}}{\hbar} \left(\frac{e^{i\omega t} + e^{-i\omega t}}{2} \right) e^{-i\omega_0 t} c_b$$

$$\dot{c}_b = -\frac{iV_{ba}}{\hbar}\left(\frac{e^{i\omega t}+e^{-i\omega t}}{2}\right)e^{i\omega_0 t}c_a$$

We then make what is known as the rotating wave approximation, we drop the $\omega+\omega_0$ terms:

$$\dot{c}_a = -\frac{iV_{ab}}{\hbar}e^{i(\omega-\omega_0)t}c_b$$

$$\dot{c}_b = -\frac{iV_{ba}}{\hbar}e^{i(\omega_0-\omega)t}c_a$$

These are solvable! We take a time derivative of the second equation:

$$\ddot{c}_b = -\frac{i}{\hbar}\frac{V_{ba}}{2}\left(i(\omega_0-\omega)e^{i(\omega_0-\omega)t}c_a + e^{i(\omega_0-\omega)t}\dot{c}_a\right)$$

We can then eliminate the a terms via substitution, which will get us terms only involving b:

$$\ddot{c}_b - i(\omega_0-\omega)\dot{c}_b + \frac{|V_{ab}|^2}{4\hbar^2}c_b = 0$$

Which is solved by

$$c_b = Ae^{\lambda t}$$

We can then solve this, and we find that

$$\lambda_\pm = \left[i\left(\frac{\omega-\omega_0}{2}\right) \pm \frac{1}{2}\sqrt{-(\omega-\omega_0)^2 - \frac{|V_{ab}|^2}{\hbar^2}}\right]$$

We note that this is imaginary, and thus we will have oscillating solutions, not decaying or growing solutions (we can factor out an i from the whole thing). We can put together the whole solution, which is a linear combination of the two solutions:

$$c_b = Ae^{\lambda_+ t} + Be^{\lambda_- t} = e^{i(\omega-\omega_2)t/2}\left[Ae^{i\omega_r t} + Be^{-i\omega_r t}\right]$$

If we now reintroduce the initial condition that $c_a(0)=1$ and $c_b(0)=0$ (we start in the a state), we find that

$$c_b(t) = e^{i(\omega-\omega_0)t/2}\left[i(A-B)\sin\omega_0 t\right] = De^{i(\omega-\omega_0)t/2}\sin(\omega_r t)$$

Where $D = i(A-B)$. It can be shown that $D = -\frac{V_{ba}}{2\hbar\omega_r}$, from the initial conditions. We can compute the magnitudes, and we can find that

$$P_{a\to b} = \frac{|V_{ba}|^2}{\hbar^2\left[(\omega-\omega_0)^2 + \frac{|V_{ba}|^2}{\hbar^2}\right]}\sin^2\omega_r t$$

Suppose we had an $\mathbf{E} = E_0\cos\omega t$ in the $\hat{z}$ direction. If the particle has charge, then the force would be $\mathbf{F} = qE_0\cos\omega t\,\hat{z}$. The potential energy $E_{\text{Pot}} = -\int\mathbf{F}\cdot dz = -qzE_0\cos\omega t$, which is the V that we call the potential. We can then compute the matrix element H'_{ab}:

$$H'_{ab} = \int e^{i\omega_0 t}\psi_a^*(q)H'(q,t)e^{-i\omega_0 t}\psi_b(q)\,dq = H'_{ab}(t)$$

Where q is the generalized coordinate. From here, we can sub that in, by separating the spatial and time components, $H'_{ab} = V'_{ab}\cos\omega t$:

$$\dot{c}_a = -\frac{i}{\hbar}(V'_{ab}\cos\omega t)e^{-i\omega_0 t}c_b$$

$$\dot{c}_b = -\frac{i}{\hbar}(V'_{ba}\cos\omega t)e^{+i\omega_0 t}c_a$$

We now make the assumption that $\omega - \omega_0 \ll \omega + \omega_0$, known as the rotating wave approximation:

$$\ddot{c}_b - i(\omega_0 - \omega)\dot{c}_b + \frac{|V'_{ab}|^2}{4\hbar}c_b = 0$$

Let us do a summary so far. We have some H such that $H = H^0(q) + H'(q,t)$, where q is some generalized coordinate. We have a two-level system, so we have two eigenstates, ψ_a and ψ_b, such that

$$H^0\psi_{a/b} = E_{a/b}\psi_{a/b}$$

We also have that ψ_a and ψ_b are complete and orthonormal. This means that we can construct a general solution:

$$\Psi(q,t) = c_a(t)e^{-iE_a t/\hbar}\psi_a(q) + c_b(t)e^{-iE_b t/\hbar}\psi_b(q)$$

From this, we can rewrite the Schrodinger equation as a pair of equations:

$$\dot{c}_a(t) = -\frac{i}{\hbar}H'_{ab}e^{-i\omega_0 t}c_b$$

$$\dot{c}_b(t) = -\frac{i}{\hbar}H'_{ba}e^{i\omega_0 t}c_a$$

Where $\omega_0 = \frac{E_b - E_a}{\hbar}$, and we have that $\langle a|H'|a\rangle = 0$ and $\langle b|H'|b\rangle = 0$. If this is true, this is exact, otherwise we have extra terms.

Suppose we have a first order, small interaction. In this case, we have that

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

Suppose that a and b are levels in an atom, and we have that $\mathbf{E} = E_0\hat{z}\cos(\omega t)$. Note that we are assuming that $\lambda \gg$ the atom size. We can then find the Hamiltonian:

$$H' = -\int q\mathbf{E}\cdot d\hat{z} = -qE_0 z\cos(\omega t)$$

We can then compute V'_{ab}:

$$V'_{ab} = \iiint \psi_a^*(-qE_0 z)\psi_b\, d^3\mathbf{r} = -E_0\iiint \psi_a^*(qZ)\psi_b d^3\mathbf{r}$$

This is known as the polarization, and is denoted using $\mathcal{P}$. If we then compute the probability, we will have

$$P_{a\to b} = \left(\frac{|\mathcal{P}|E_0}{\hbar}\right)^2\frac{\sin^2\left[(\omega_0 - \omega)\frac{t}{2}\right]}{(\omega_0 - \omega)^2}$$

This is known as stimulated absorption, a wave packet comes in, excites the state up a state, and then a wave packet leaves with less energy. Since the probabilities are squared, this means that the opposite is the same, which is known as stimulated emission. A lower energy wavepacket comes in, drops the state from high energy to low energy, and then a wavepacket leaves with higher energy. We note that if we have more particles in the upper state than in the lower state, we see that absorption does nothing, but emission generates 2 photons. This means that we can use it to amplify the input. This is the basis for masers and lasers.

Suppose instead we have an incoherent driving signal, such as different frequencies, different polarizations, and different directions. To do this, we use approximations that average over ω and space.

Let's do some E and M. If we have a travelling electric field:

$$\mathbf{E} = \hat{z}E_0 \cos(kx - \omega t)$$

We can compute the **B** field:

$$\mathbf{B} = B_0 \hat{x} \cos(kx - \omega t)$$

Where $B_0 = \frac{E_0}{c}$. The energy per unit volume in an **E** field, is $\frac{1}{2}\varepsilon_0 E_0^2 \cos^2(kx - \omega t)$. We can do the same thing for the **B** field, $\frac{1}{2}\mu_0 B_0^2 \cos^2(kx - \omega t)$.

The average energy per unit volume in an EM field with fixed frequency is given by

$$u = \frac{\varepsilon_0 E_0^2}{2}$$

We can then rewrite the transition probability in terms of the energy density:

$$P_{a\to b} = \frac{2u(\omega)}{\varepsilon_0 \hbar^2} |\mathcal{P}|^2 \frac{\sin^2\left[(\omega_0 - \omega)\frac{t}{2}\right]}{(\omega_0 - \omega)^2}$$

We deal with a range of frequencies, known as the spectral density:

$$du(\omega) = \rho(\omega) d\omega$$

And then the total density is

$$\int du = \int_0^\infty \rho(\omega) d\omega$$

Using this when computing the transition probability:

$$P_{b\to a} = \frac{2|\mathcal{P}|^2}{\varepsilon_0 \hbar^2} \int_0^\infty \rho(\omega) \frac{\sin^2\left[(\omega_0 - \omega)\frac{t}{2}\right]}{(\omega_0 - \omega)^2} d\omega$$

After solving this integral, we have that

$$P_{b\to a} = \frac{|\mathcal{P}|^2 t}{\varepsilon_0 \hbar^2} \int_0^{-\infty} \rho(x) \frac{\sin^2 x}{x^2}\, dx$$

This interior function is peaked around $x = 0$, and since we have made the substitution $x = (\omega_0 - \omega)\frac{t}{2}$, we can rewrite this as

$$P_{b\to a} \approx -\frac{|\mathcal{P}|^2 t}{\varepsilon_0 \hbar^2} \rho(\omega_0) \int_{-\infty}^\infty \frac{\sin^2 x}{x^2}\, dx = \frac{|\mathcal{P}|^2 t \pi}{\varepsilon_0 \hbar^2} \rho(\omega_0)$$

Suppose you have a bunch of atoms, and we start at $t = 0$, with $P_a = \frac{3}{4}$ and $P_b = \frac{1}{4}$. We note that based on the fact that the probabilities of transition both ways are the same, then we shouldn't have any changes in the probability! What are we missing?

Suppose we have a hollow box with metal walls. If we have this setup, the electric field at the walls must be $\mathbf{E} = 0$. If we use Maxwell's equations, we find that

$$|\mathbf{E}| = E_n \left[\sin \frac{m_x \pi x}{l} \sin \frac{m_y \pi y}{l} \sin \frac{m_z \pi z}{l}\right] \cos \omega t$$

Each mode n is a harmonic oscillator, and we have that

$$E_{nm} = \left(n_m + \frac{1}{2}\right) \hbar \omega_n$$

We find that even at $T = 0$, $\rho(\omega) \neq 0$, and the rate of emission is given by

$$R_{b \to a} = \frac{\omega_0}{3\pi \varepsilon_0 \hbar c^3} |\mathcal{P}|^2$$

Essentially, we thought that the Schrodinger equation would tell us that our probabilities would not change, but our system is coupled to a bunch of harmonic oscillators (in the ground state) of varying frequencies. Since the oscillators are in the ground state, there is no stimulated absorption, but we have stimulated emission, as we expect.

8 Summary

We begin with talking about Hilbert spaces. We can write a state as a ket:

$$|S(t)\rangle$$

This is the quantum state of the system, and carries all the information about the system that we can know. We need to know about time evolution and prediction/measurement. Time evolution is given by the $\hat{H}$ operator:

$$\hat{H} |S(t)\rangle = i\hbar \frac{\partial}{\partial t} |S(t)\rangle$$

We have that for any observable O, there is an operator $\hat{O}$ that has eigenstates and eigenvalues such that $O |O_n\rangle = \lambda_n |O_n\rangle$. We also know that α_n are the only possible results of a measurement. If we normalize the vectors, $\langle O_n | O_m \rangle = \delta_{nm}$, then we can write any $|S(t)\rangle$ as a linear combination:

$$|S(t)\rangle = \sum \lambda_n |O_n\rangle$$

And the probability of measuring $|O_n\rangle$ is $P_n = |\lambda_n|^2$. Orthonormality and completeness are at the heart of everything we see in this class. We can talk more about bras and kets, and define an inner product, $\langle f | g \rangle = \int f^* g \, dx$. If we have that $\langle \alpha | \alpha \rangle = 1$, which means that this is normalized. We also have a projection operator, $\hat{P}_\alpha = |\alpha\rangle \langle \alpha|$. We also have that the identity operator is

$$\hat{1} = \sum_n |n\rangle \langle n|$$

We can do the same thing for continuous variables:

$$\hat{1} = \int |n\rangle \langle n| \, dn$$

These come in handy when we need to change bases, and we can insert in the identity to rewrite things.

We then dealt with addition of angular momentum, and dealing with multiple particles. The states $|S, m\rangle$ are defined by the total spin, S, and m is spin along a certain axis. These states have the following properties:

$$\hat{S}^2 |S, m\rangle = \hbar^2 S(S+1) |S, m\rangle$$
$$\hat{S}_z |S, m\rangle = m\hbar |S, m\rangle$$

where m varies from $-S$ to S in steps of 1. The challenge is finding a way to create total angular momentum operators (that can cover both spin and orbital angular momentum). We can, using the raising and lowering operators:

$$S_\pm |S, m\rangle = \hbar\sqrt{S(S+1) - m(m\pm 1)}\, |S, m\pm 1\rangle$$

If we do this for two electrons, we see that there are 4 states that are orthonormal and obey these rules, the triplet states and the singlet state. We represent the states via $|S_{\text{total}}, m_{\text{total}}\rangle$:

$$|1,1\rangle = |\uparrow\rangle \otimes |\uparrow\rangle$$
$$|1,0\rangle = \frac{1}{\sqrt{2}} (|\uparrow\rangle \otimes |\downarrow\rangle + |\downarrow\rangle \otimes |\uparrow\rangle)$$
$$|1,-1\rangle = |\downarrow\rangle \otimes |\downarrow\rangle$$
$$|0,0\rangle = \frac{1}{\sqrt{2}} (|\uparrow\rangle \otimes |\downarrow\rangle - |\downarrow\rangle \otimes |\uparrow\rangle)$$

We then move from this to multiple particles. We want to generalize the idea of the classical Hamiltonian to multiple particles

$$H = \frac{|\mathbf{p}_1|^2}{2m_1} + \frac{|\mathbf{p}_2|^2}{2m_2} + V(\mathbf{r}_1, \mathbf{r}_2)$$

We do the standard canonical quantization, where we replace the momentums:

$$\hat{H} = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\mathbf{r}_1, \mathbf{r}_2)$$

We can then write the Schrodinger equation:

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}_1, \mathbf{r}_2, t)$$

We cna do this via separation of variables, with $\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \psi(\mathbf{r}_1, \mathbf{r}_2)\phi(t)$, which gets that

$$\phi(t) = e^{-iEt/\hbar}$$

$$\hat{H}\psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2)$$

If the particles are non-interacting, we separate the potential, $V(\mathbf{r}_1, \mathbf{r}_2) = V(\mathbf{r}_1) + V(\mathbf{r}_2)$. From this, we find that $E = E_1 + E_2$ (via separation of variables), $\hat{H}_1\psi_1 = E_1\psi_1$, and $\hat{H}_2\psi_2 = E_2\psi_2$.

if the particles are identical, any measurable property is invariant under particle swap. If we have some $\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \ldots, t)$, and we interchange $\mathbf{r}_1$ and $\mathbf{r}_2$:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \ldots, t) = \pm\Psi(\mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_4, \ldots, t)$$

Whether it is a plus or minus is dependent on the type of particle. For Bosons, we have $+$, and for Fermions we have the $-$. If we have two non-interacting particles, where we can separate the potential, and then separate the wavefunction $\Psi = \Psi_a\Psi_b$:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = A\left(\Psi_a(\mathbf{r}_1, t)\Psi_b(\mathbf{r}_2, t) \pm \Psi_a(\mathbf{r}_2, t)\Psi_b(\mathbf{r}_1, t)\right)$$

Let us now look at electrons, which are spin-$\frac{1}{2}$ particles. Schematically, we can write a system of 2 electrons as

$$\Psi(1, 2)\chi(1, 2)$$

representing the spatial and spin parts of the wavefunction. If we interchange particles, we get $\Psi(2, 1)\chi(2, 1)$, and we expect (since they are Fermions) that we will have a sign change in one of the terms, not both. This means that we expect that either the spin or the spatial part will flip signs while the other will remain the same. We also note that if we look at the triplet states, they are bosonic, they don't flip signs, while the singlet state is fermionic.

We then move to the periodic table, where the energy of the Hydrogen atom has a dependence on e^2. For heavier elements, any time that we have an e^2, we change that to Ze^2. Thus for a heavier element, we have $-z^2E_{H0}\frac{1}{n^2}$, where we let the ground state be 13.6 eV. When we fill the orbitals, we fill from smallest orbital, until it is full, and then work up to the next layer, although this does eventually breaks.

If we have N electrons in the system, we can find the max filled shell, n_{Fermi}, which then leads to E_{Fermi}. We can then compute the ground state energy via an integral, taking into account spin as well as the dimension of the problem. In 1 dimension:

$$E_0 = \sum_n E_n \to \int E_n\, dn$$

Looking at periodic potentials, we can use the Bloch theorem, which states that we can get the physics given a shift by just adding a phase exponential.

We then move into (non-degenerate) perturbation theory, which hinges on completeness and orthonormality. We define our Hamiltonian as

$$HH^0 + H^1$$

Where we know the eigenvalues and eigenfunctions of H^0, $H^0\left|\psi_n^0\right\rangle = E_n^0\left|\psi_n^0\right\rangle$, which are orthonormal and complete. We assume that the solution will be of the form:

$$\left|\psi_n\right\rangle = \left|\psi_n^0\right\rangle + \lambda\left|\psi_n^1\right\rangle + \lambda^2\left|\psi_n^2\right\rangle + \ldots$$

We then know that $H\left|\psi_n\right\rangle = E_n\left|\psi_n\right\rangle$, which we can then combine with the Hamiltonian definition and the assumption for the wavefunction. We can then group terms by order, which gives us different equations. The λ^0 terms just give back the Schrodinger equation, and the λ terms give

$$H^1\left|\psi_n^0\right\rangle + H^0\left|\psi_n^1\right\rangle = E_n^0\left|\psi_n^1\right\rangle + E_n^1\left|\psi_n^0\right\rangle$$

We can then apply a $\langle\psi_m^0|$ to both sides of the zeroth and first order equations, which leaves us with

$$E_n^1 = \langle\psi_n^0|H^1|\psi_n^0\rangle$$

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

This gives the first order corrections to the energy and the wavefunction, which we see rely on matrix elements. We also note that this only works for non-degenerate perturbation theory because the denominator of the wavefunction corrections could be zero if we had degenerate energies.

In the degenerate case, we have two degenerate states, ψ_a^0 and ψ_b^0, so we define $|\psi_n^0\rangle = \alpha|\psi_a^0\rangle + \beta|\psi_b^0\rangle$. We then find that the degeneracy is usually broken. We then take inner products with both of the wavefunctions, and we get two equations, which can then be represented as a matrix equation. From this, we find that

$$E_\pm^1 = \frac{1}{2}\left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb}) + 4|W_{ab}|^2}\right]$$

Now moving to time-dependent perturbation theory, we have

$$H = H^0(x) + H^1(x,t)$$

where the first Hamiltonian can rely on anything except time. We know that H^0 has a set of complete and orthonormal solutions, which we will use. For a two level system, we have the basis formed by ψ_a and ψ_b, so we can define our general state as

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

The probability of being in either state will just be the magnitude of the coefficients. We can then insert the general state into the time-dependent equation:

$$H|\Psi(x,t)\rangle = i\hbar\frac{\partial}{\partial t}|\Psi(x,t)\rangle$$

From this (by taking inner product on both sides with $\langle\psi_a|e^{iE_at/\hbar}$ and the corresponding state for b), we can get the equations:

$$\dot{c}_a(t) = -\frac{i}{\hbar}H_{ab}^1 e^{-i\omega_0 t}c_b(t)$$

$$\dot{c}_b(t) = -\frac{i}{\hbar}H_{ba}^1 e^{-i\omega_0 t}c_a(t)$$

Where $\omega_0 = \frac{E_b - E_a}{\hbar}$. We can solve this iteratively or using the rotating wave approximation.

When perturbation theory doesn't work, like if the whole Hamiltonian is not solvable, we have two things that might help. The first is the Variational Principle, in which we guess at a ψ, which has some parameter that we can vary. We then normalize this, and then use the fact that

$$\langle\psi|H|\psi\rangle \geq E_{gs}$$

We can then compute this, and then minimize the left side by twiddling the parameter.

Finally, let us do a summary of WKB. If $V(x)$ is a constant, V, the Schrodinger equation solutions will be either complex or real exponentials, depending on whether E is greater than or less than V. WKB shows that our solutions will be generalized exponentials where we replace p with an integral.