Second Quantization

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1 Baby Steps

We start our journey into second quantization with a question. How do we do quantum mechanics on systems with multiple fermions? Well, we are looking for a many body wavefunction ψ that represents our quantum states. We also have a set of particles and allowed states for these particles. We can label these particle states by a quantum number which we'll call E_i. So we can say $\phi_{E_i}(\vec{r})$ is an allowed single particle state. We can then represent our full many body wavefunction by superimposing these ϕ:

$$\psi(r_1, r_2, r_3, ..., t) = \sum_{(E_1, E_2, ..., E_N)} c(E_1, E_2..., t)\phi_{E_1}(r_1)\phi_{E_2}(r_2)...\phi_{E_N}(r_N)$$

In this case we have N particles that populate our set of single particle states. There's just one issue these are fermions, so we need to have a fully antisymmetric wavefunction under particle interchange. In theory this condition is represented in our $c(E_1, E_2, ..., t)$ coefficient. The issue with this is that its hard. We'll get into how we can antisymmetrize later but you end up with a gigantic wavefunction because for every state one particle occupies all the other particles need to be able to occupy it equally as we are working with identical particles.

We need a way to make calculations on systems with many particles more tractable, we want a system that more easily respects the fact that our particles are indistinguishable. That's where second quantization comes in. We are going to move to describing our quantum states by a set of numbers $\{n_1, n_2, ..., n_\infty\}$ with $n_i = 0$ or 1 that describe the occupation of state i. However, to do this transformation we'll have to do some work to antisymmetrize our wavefunction before we can simplify it. Now we'll rewrite our ψ. We can rewrite our sum over all arrangements and sets of quantum numbers E_i in a nice way. We can first consider a set of E_i, so a set that describes N distinct states which will each be occupied. We can then sum over all the permutations of this set to represent the different ways our particles can be arrranged. Mathematically this looks like:

$$\psi = \sum_{E_i \text{ sets}} \sum_{\text{permutations}} c\phi_1...\phi_N$$

Essentially we first pick the states that get occupied than sum over all the different ways the states can be occupied. Now lets hone in on the permutation sum for a second. It looks like:

$$c(E_1, E_2, E_3, ..., E_N, t)\phi_{E_1}(\vec{r}_1)...\phi_{E_N}(\vec{r}_N) + c(E_2, E_1, E_3, ..., E_N, t)\phi_{E_2}(\vec{r}_1)...\phi_{E_N}(\vec{r}_N) + ...$$

Now we can say that because we have identical particles there shouldn't be a different magnitude for the different permutations so that the absolute value of all the c's is the same and they only amount to a sign difference. Because of this we can factor out the first c and we'll end up with something like:

$$c(E_1, E_2, E_3, ..., E_N, t)(\phi_{E_1}(\vec{r}_1)...\phi_{E_N}(\vec{r}_N) - \phi_{E_2}(\vec{r}_1)...\phi_{E_N}(\vec{r}_N) \pm ...)$$

This c that we just factored out has a magnitude that is fully determined by just the set of quantum numbers we are working with. This set of quantum numbers is just a set of occupied states. Because of this we can say:

$$c(E_1, E_2, ..., E_N, t) \propto f(n_1, n_2, ..., n_\infty, t)$$

Our c should just be a function of which state is occupied (and time) with a sign set by the fact that we factored it out of the first permutation. Now we recognize that the sum that the c multiplied was our antisymmetric combination of occupied states which is just given by the slater determinant:

$$\begin{vmatrix} \phi_{E_1}(\vec{r}_1) & ... & \phi_{E_1}(\vec{r}_N) \\ ... & ... & ... \\ \phi_{E_N}(\vec{r}_1) & ... & \phi_{E_N}(\vec{r}_N) \end{vmatrix}$$

Which from now on we'll call $SD(n_1, ..., n_\infty)$. Using this we can write our state as:

$$\psi = \sum_{\{n_1,...,n_\infty\}} f(n_1, ..., n_\infty, t) \frac{1}{\sqrt{N!}} SD(n_1, ..., n_\infty)$$

Essentially we took our permutations and shoved them into this slater determinant to capture antisymmetrization information and then we took f and the square root $N!$ out to capture information about the prevalance of that state in the many body wavefunction where we are now summing over all possible sets of occupation numbers. In this framing its very clear that we don't care about which particle is which we just care about which states are occupied which is all that matters for the physics.

2 Hilbert Space!? I WANT ENGLISH FOUR EYES

Using this we see how we can describe our full space by the occupation of certain states using the basis functions in the sum from the end of the last section. We can represent an arbitrary basis occupation state by the ket below:

$$|n_1, n_2, ..., n_\infty\rangle$$

Now we are going to introduce two very important operators, a_i and $a_i^\dagger$. These operators are technically defined by their algebra but the algebra is trivial from the real defining property which is that $a_i^\dagger$ take a state n_i from unoccupied to occupied, or occupied to 0. While the inverse is true for a_i which takes occupied to unoccupied or unoccupied to 0. From this we can say we have the relations:

$$\{a_i, a_j^\dagger\} = a_i a_j^\dagger + a_j^\dagger a_i = \delta_{ij}$$

$$\{a_i, a_j\} = \{a_i^\dagger, a_j^\dagger\} = 0$$

The first just comes from the fact that if we create and destroy at the same place we get the identity while working with different states gives us 0 (this is not trivial and is part of why we define the operator by the commutation relation). We then have that if we create twice or annihilate twice we get nothing no matter what (again the fact that this holds for different particle states is non-trivial and leads to this definition being important). But the key here is the fact that these operators do let you raise and lower. Using these we write:

$$|n_1, ..., n_\infty\rangle = (a_1^\dagger)^{n_1} (a_2^\dagger)^{n_2} ... (a_\infty^\dagger)^{n_\infty} |0\rangle$$

Now consider acting on this with a_k, if $n_k = 0$ we could just commute a_k to $|0\rangle$ to get 0, but if $n_k = 1$ we could commute this a_k to $a_k^\dagger$. Our anticommutation relation tells us that

$a_i a_j^\dagger = -a_j^\dagger a_i$ so we pick up as many minus signs as commutations we do. This means that we get:

$$a_k|n_1, ..., n_\infty\rangle = (-1)^{\Sigma_k}(a_1^\dagger)^{n_1}(a_2^\dagger)^{n_2}...a_k a_k^\dagger...(a_\infty^\dagger)^{n_\infty}|0\rangle$$

$$\Sigma_k = n_1 + n_2 + ... + n_{k-1}$$

This just gives 0 if $n_k = 0$. Now we can use the fact that:

$$a_k a_k^\dagger = 1 - a_k^\dagger a_k$$

If we plug this in to our earlier equation we get:

$$a_k|n_1, ..., n_\infty\rangle = (-1)^{\Sigma_k}(a_1^\dagger)^{n_1}(a_2^\dagger)^{n_2}...(1 - a_k^\dagger a_k)...(a_\infty^\dagger)^{n_\infty}|0\rangle$$

The term on the right is a_k which can just be commuted to $|0\rangle$ to give us 0 so that term dies. This means we are just left with:

$$a_k|n_1, ..., n_\infty\rangle = (-1)^{\Sigma_k}(a_1^\dagger)^{n_1}(a_2^\dagger)^{n_2}...(a_\infty^\dagger)^{n_\infty}|0\rangle$$

We can account for the fact that our answer changes based on n_k by including it in our formula:

$$a_k|n_1, ..., n_\infty\rangle = (-1)^{\Sigma_k}\sqrt{n_k}|n_1, ..., n_k - 1, ..., n_\infty\rangle$$

In this case we get 0 if we have $n_k = 0$ and our previous result if $n_k = 1$ like we want. You can repeat the exact same process and logic to get:

$$a_k^\dagger|n_1, ..., n_\infty\rangle = (-1)^{\Sigma_k}\sqrt{1 - n_k}|n_1, ..., n_k + 1, ..., n_\infty\rangle$$

This tells us how our annihilation and creation operators act on our states. This is going to be very important for the next section where we learn that representing operators in this formalism will require these operators.

3 I'm Looking For An Equation... A Schroedinger Equation

Let us return to our many body wavefunction for a second:

$$\psi = \sum_{\{n_1,...,n_\infty\}} f(n_1, ..., n_\infty, t)\frac{1}{\sqrt{N!}}SD(n_1, ..., n_\infty)$$

We have our system governed by the many body Hamiltonian:

$$\hat{H} = \sum_{i=1}^{N} T(\vec{r}_i, \dot{\vec{r}}_i) + \frac{1}{2}\sum_{i,j=1,i\neq j}^{N} V(\vec{r}_i, \vec{r}_j)$$

Where the factor of $1/2$ accounts for the fact that we are double counting in this sum as each i, j has a corresponding j, i. We can say that we satisfy the Schroedinger equation:

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi$$

We want to plug in our new occupation state picture into this equation. I'll start by writing:

$$|\psi\rangle = \sum_{n_1,...,n_\infty} f(n_1, ..., n_\infty, t)|n_1, ..., n_\infty\rangle$$

We can then write the left hand side of the Schroedinger eq. as:

$$i\hbar\frac{\partial|\psi\rangle}{\partial t} = i\hbar\sum_{n_1,...,n_\infty}\frac{\partial f}{\partial t}|n_1,...,n_\infty\rangle$$

This gives us:

$$i\hbar\sum_{n_1,...,n_\infty}\frac{\partial f}{\partial t}|n_1,...,n_\infty\rangle = \hat{H}\sum_{n_1,...,n_\infty} f(n_1,...,n_\infty,t)|n_1,...,n_\infty\rangle$$

Now we left multiply by a state corresponding to a fixed $n_1, n_2, ..., n_\infty$. On the left hand side we only have scalars multiplying our state so orthonormality tells us the left hand side becomes:

$$i\hbar\frac{\partial f(n_1,...,n_\infty,t)}{\partial t}$$

Now we look to the right hand side. We'll start by looking at the kinetic part of the Hamiltonian $\hat{T}$ which only acts on a single particle. To actually do this calculation we'll bring back the Slater determinant and rewrite it as:

$$\frac{SD(n_1,...,n_\infty)}{\sqrt{N!}} = \frac{1}{\sqrt{N!}}\sum_{\tilde{p}}(-1)^{\tilde{p}}\hat{P}\phi_{E_1}(\vec{r}_1)...\phi_{E_N}(\vec{r}_N)$$

Where $\hat{P}$ is an operator that permutes the order of the electrons and $\tilde{p}$ determines the amount of permutations (and thus the sign of the corresponding term). Right now we are interested in matrix elements of $\hat{T}$ and their sum over all particles. Writing this out we get:

$$\sum_{i=1}^{N}\sum_{n'_1,...,n'_\infty}\frac{1}{N!}f(n'_1,...,n'_\infty,t)\langle n_1,...,n_\infty|\hat{T}(\dot{r}_i)|n'_1,...,n'_\infty\rangle$$

Where we have just written out the first term of the Hamiltonian acting on our state after left multiplying by $\langle n_1,...,n_\infty,t|$. If we write this using our Slater determinant notation from earlier we get:

$$\sum_{i=1}^{N}\sum_{n'_1,...,n'_\infty}\sum_{p,p'}\frac{1}{N!}f(n'_1,...,n'_\infty,t)\int\hat{P}\phi_{E_1}(r_1)...T(\dot{r}_i)\hat{P}'\phi_{E'_1}(r_1)...dr_1...dr_N$$

Notice that our $\hat{T}$ only acts on a single particle which means most of the integrals can be done separately leaving us with just one integral. We also know that this means the only thing that can happen is a single particle transitions to another state which means this can only be non zero if our $n_1,...,n_\infty$ and $n'_1,...,n'_\infty$ differ in at most two places. So for a given particle we'll just be left with the integral over that particle's two states with the sum over occupations killed by the fact that the state we inner product with only selects two new states. Noting all of this we can rephrase the expression above. We can write our sum as a sum over possible transitions from one state being occupied to another which is the only thing that's allowed to happen. Because we don't care about which particle is making the transition we can sum over all of the possible ways particles can make that transition which will cancel out the $N!$ to give us:

$$\sum_{k,l}(-1)^{\Sigma_k+\Sigma_l}\int\phi^*_{E_k}(r)T(\dot{r})\phi_{E_l}(r)f(n_1,...,n_k-1,n_l+1,...,n_\infty,t)dr$$

Where k, l represent the states we transition from and to respectively for a given set of occupation numbers. Now consider the ket below:

$$\sum_{n'_1,...,n'_\infty} \hat{T} f|n'_1, ..., n'_\infty\rangle$$

We could re-express it in the same basis as:

$$\sum_{n_1,...,n_\infty} \sum_{n'_1,...,n'_\infty} f(n'_1, ..., n'_\infty)\langle n_1, ..., n_\infty|\hat{T}|n'_1, ..., n'_\infty\rangle|n_1, ..., n_\infty\rangle$$

But we just learned that we can rewrite this to get:

$$\sum_{n_1,...,n_\infty} \sum_{k,l} \langle k|T|l\rangle f(n_1, ..., n_k = 0, ..., n_l = 1, ..., n_\infty, t)(-1)^{\Sigma_k+\Sigma_l}|n_1, ..., n_k = 1, ..., n_l = 0, ..., n_\infty\rangle$$

Where we select our pair so that $n_k = 1$ and $n_l = 0$ is the starting point. However, we can note that:

$$(-1)^{\Sigma_k+\Sigma_l}|n_1, ..., n_k, ..., n_l, ..., n_\infty\rangle = a_k^\dagger a_l|n_1, ..., n_k - 1, ..., n_l + 1, ..., n_\infty\rangle$$

Plugging this in and moving everything that can be outside of our sum over $n_1, ..., n_\infty$ we get:

$$\sum_{k,l} \langle k|T|l\rangle a_k^\dagger a_l \sum_{n_1,...,n_\infty} f(n_1, ..., n_\infty)|n_1, ..., n_\infty\rangle = \sum_{k,l} \langle k|T|l\rangle a_k^\dagger a_l|\psi\rangle$$

Using this we can write our Schroedinger equation as:

$$i\hbar \frac{\partial|\psi(t)\rangle}{\partial t} = \sum_{k,l} \langle k|T|l\rangle a_k^\dagger a_l|\psi\rangle + \text{interaction terms}$$

The key here is that we are breaking up our Hamiltonian into a set of matrix elements where the only actual operators acting are the raising and lowering operators which are generally easier to find and work with than most other things. We can repeat this exact same procedure with our potential term but this time we have to enumerate all possible two particle transitions (as two particles interact in that case), that will lead us to get:

$$\hat{H} = \sum_{k,l} \langle k|T|l\rangle a_k^\dagger a_l + \frac{1}{2} \sum_{k,l,s,t} \langle k, l|V|s, t\rangle a_k^\dagger a_l^\dagger a_t a_s$$

This lets us represent a very general many body Hamiltonian just by using raising and lowering operators. We can just plug this in to get our Schroedinger equation in our particle number picture as this form very clearly shows how the Hamiltonian acts on our particle number states. To talk about how we generally second quantize an operator we need to define the field operator:

$$\hat{\psi}(r) = \sum_k \phi_k(r) a_k$$

Where ϕ_k are our single particle states and a_k is our destruction operator. Now to second quantize a single particle operator like $T(\dot{r}_i)$ we just take $r_i \to r$ and then sandwich T between $\hat{\psi}^\dagger$ and $\hat{\psi}$ and integrate over all space. For a two particle operator like V we would let $r_i \to r$, $r_j \to r'$ and sandwich between $\hat{\psi}^\dagger(r)\hat{\psi}^\dagger(r')$ and $\hat{\psi}(r)\hat{\psi}(r')$ and integrate over all space over both coordinates. You can repeat this for an arbitrary particle interaction to second quantize any Hamiltonian.