L12 – IDENTICAL PARTICLES, PERTURBATION, AND ENTANGLEMENT

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1. Two Particles

For two particles, the spatial wave function should be written as

$$\Psi(\vec{x}_1, \vec{x}_2, t)$$

If we include the spin wave function (spinor), it can be written as

$$\Psi_{m_{s1} m_{s2}}(\vec{x}_1, \vec{x}_2 t)$$

where m_{s1}, m_{s2} are spin coordinates, being indices running over the possible z components of the spins, but for now, let us not worry about the spin part too much, and use the first form. The general Hamiltonian can be written as

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

The wave function gives the probability to find particle 1 within volume dV_1 and particle 2 within volume dV_2 as:

$$P(dV_1, dV_2) = |\Psi(\vec{x}_1, \vec{x}_2, t)|^2 dV_1 dV_2$$

Here dV_1 can be $dx_1 dy_1 dz_1$ or any other volume element that you may express in other coordinate systems. The probability sum rule is

$$\int |\Psi(\vec{x}_1, \vec{x}_2, t)|^2 dV_1 dV_2 = 1$$

Formally, finding stationary states and expanding an arbitrary state in terms of stationary states proceed exactly the same way as in one particle problem. The stationary state satisfies

$$\hat{H}\psi(\vec{x}_1, \vec{x}_2) = E\psi(\vec{x}_1, \vec{x}_2)$$

and

$$\psi(\vec{x}_1, \vec{x}_2, t) = \exp(-iEt/\hbar)\psi(\vec{x}_1, \vec{x}_2, t = 0)$$

Any wave function $\Psi(\vec{x}_1, \vec{x}_2, t)$ can be expressed as a linear combination (integral for continuous E values and sum for discrete E values) of $\psi_E(\vec{x}_1, \vec{x}_2)$.

2. Identical Particles

Consideration of more than one particle is essential in order to apply QM to real systems. In this context, the notion of identical particles emerges as another essential difference between CM and QM. In CM, each particle can be labeled and "followed." In QM, this is not possible. All electrons are *identical*. Likewise, all protons are *identical*. For a given pool of N fundamental particles, there is absolutely no way to distinguish which one is which. As such, asking "which" does not make sense.

The meaning of these statements is the following. In CM, we can have this baseball and that baseball. They might look very similar to each other, but we can label them somehow without affecting the CM physics of each baseball. We can do this by imprinting a serial number on each baseball, inside the hide before sewing it, if you like. If we have a bag full of such baseballs, and if we pick one baseball at random, we can always identify the ball by its serial number. In this sense, each ball is different and not identical. For fundamental particles, this is not possible, since we simply cannot label them. Let us say that there are two electrons in an atom, in analogy with two baseballs in a bag. Using UV light, we can kick one of the two electrons out. When we do, we absolutely do not know which of the two electrons it is. In fact, the question itself is meaningless. What does it mean "which of the two"? All we know is that there are two electrons in the atom, and when we took one out, there is one electron left.

The identical nature of fundamental particles is summarized in the following *law of exchange symmetry*:

$$\begin{aligned} \text{Two fermions :} \quad & \Psi(\vec{x}_1, \vec{x}_2) = -\Psi(\vec{x}_2, \vec{x}_1) \\ \text{Two bosons:} \quad & \Psi(\vec{x}_1, \vec{x}_2) = \Psi(\vec{x}_2, \vec{x}_1) \end{aligned}$$

If you include the spin part

$$\begin{aligned} \text{Two fermions :} \quad & \Psi_{m_{s1},m_{s2}}(\vec{x}_1, \vec{x}_2) = -\Psi_{m_{s2},m_{s1}}(\vec{x}_2, \vec{x}_1) \\ \text{Two bosons:} \quad & \Psi_{m_{s1},m_{s2}}(\vec{x}_1, \vec{x}_2) = \Psi_{m_{s2},m_{s1}}(\vec{x}_2, \vec{x}_1) \end{aligned}$$

Here, t is implicit and fixed. This law can be generalized for many (≥ 2) particles. *The wave functions of many particles should be symmetric on exchange of two coordinates (position and spin) for bosons, while anti-symmetric for fermions.*

The correct interpretation of the above law is the following. $\vec{x}$ and m_s are the collective coordinates of the particle. Due to the identical nature of particles, it should not matter whether to use $(\vec{x}_1, m_{s1})$ for one particle and $(\vec{x}_2, m_{s2})$ for the other particle, or the other way around. Thus, in general one expects that $\Psi_{m_{s1},m_{s2}}(\vec{x}_1, \vec{x}_2) = \exp(i\theta)\Psi_{m_{s2},m_{s1}}(\vec{x}_2, \vec{x}_1)$, as the overall phase has no measurable consequence. Nature appears to choose the special phases $\theta = 0$ (fermions) and $\theta = \pi$ (bosons)[1]. Notice that we have defined fermions and bosons in the previous lecture depending on what the spin value is, and so this means that the spin and the exchange symmetry are related to each other.

The wave function symmetry has consequences on particle statistics. Bosons can occupy the same quantum state, while fermions cannot. This is shown as follows. If two fermions occupy the same states, it means, by definition, $\Psi_{m_{s1},m_{s2}}(\vec{x}_1, \vec{x}_2) = \Psi_{m_{s2},m_{s1}}(\vec{x}_2, \vec{x}_1)$. On the other hand, due to the above law, $\Psi_{m_{s1},m_{s2}}(\vec{x}_1, \vec{x}_2) = -\Psi_{m_{s2},m_{s1}}(\vec{x}_2, \vec{x}_1)$. These two equalities mean $\Psi_{m_{s1},m_{s2}}(\vec{x}_1, \vec{x}_2) = 0$, i.e. this wave function cannot be. This is the so-called *Pauli exclusion principle* for fermions.

Suppose one has a set of energy eigenstates for a one particle Hamiltonian. Let us call them "single-particle eigenstates" in this paragraph, to avoid confusion. Let us consider many particles, which, for simplicity[2], we assume to be non-interacting. When there exist more than one particle, quantum statistics is dependent on the nature of the particles. To illustrate this point, consider the zero temperature. The ground state for bosons is formed when all particles occupy the lowest energy singlle-particle eigenstate. For fermions, this is an impossibility, as two fermions cannot occupy the same state. Thus, fermions and bosons are characterized by completely different *statistics*, called *Fermi-Dirac statistics* and *Bose-Einstein statistics* respectively. To learn more about consequences of these differences in statistics, you are advised to read introductory Statistical Mechanics books like Reif. Section 5.4 of Griffiths also gives a brief introduction.

To summarize, the spin quantum number implies a certain exchange symmetry, which has the implication on the statistics. This connection is referred to as the *spin-statistics theorem.* However, keep in mind that *the law of exchange symmetry* described above is more fundamental, which holds for any wave function, while the discussion of the statistics above assumes non-interacting particles.

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[1] All fundamental particles known so far are described by these two special values. In a two dimensional electron system that can be realized in certain semiconductors, however, there can be composite particles in a certain phase (fractional Quantum-Hall phase) that obey an emerging law with $\theta \neq 0, \pi$. They are examples of what are theoretically proposed as *anyons*, particles with *any* value of θ. In three dimensions, it is believed that only $\theta = 0, \pi$ are allowed.

[2] The assumption that particles do not interact is absurd, of course. However, it is not as absurd as it sounds, as it is often, while not always, the case that it is useful to progress step by step. First, assume that particles do not interact, and find all stationary states. Second, include interactions. Now, the stationary states for the non-interacting problem are no longer stationary states but they are still useful since they continue to be a natural basis for the many body Hilbert space. Calculate what the effect of interactions are on those basis states and find, almost always approximate, stationary states for the full many body problem.

Note that all the discussion here applies both to elementary particles or composite particles. The electron is an elementary fermion to the current knowledge. The photon is an elementary boson. The proton is a composite fermion, consisting of three quarks. The π meson is a composite boson, consisting of one quark and one anti-quark.

Definition 2.1. Slater Determinant

Suppose you pose the question "I have two identical fermions, and I like to fill two distinct one-particle states with them. What is the two-body wave function?" The general answer to this exists. Actually the answer exists for any number, say N, of particles, and is the so-called *Slater determinant.* It is

$$\frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_1(1) & \psi_2(1) & ... & ... & \psi_N(1) \\ \psi_1(2) & \psi_2(2) & ... & ... & \psi_N(2) \\ ... & ... & ... & ... & ... \\ ... & ... & ... & ... & ... \\ \psi_1(N) & \psi_2(N) & ... & ... & \psi_N(N) \end{vmatrix}$$

where $\psi_i(j)$ is a short-hand notation for wave function for state i with compound coordinates ($\vec{x}_j$, $m_{s,j}$). It is easy to see that when exchanging two rows the wave function acquires a minus sign, meeting the requirement for the fermion exchange symmetry.

Example 2.2. He Atom

In the He atom, two electrons occupy the 1s level. Since the spatial wave functions that the two electrons occupy are the same, they need to occupy distinct spin states, up and down, so that the two quantum states are distinct. The Slater determinant is then

$$\frac{1}{\sqrt{2}}\begin{vmatrix} \psi_{1s}(\vec{x}_1)|\uparrow\rangle & \psi_{1s}(\vec{x}_1)|\downarrow\rangle \\ \psi_{1s}(\vec{x}_2)|\uparrow\rangle & \psi_{1s}(\vec{x}_2)|\downarrow\rangle \end{vmatrix}$$

which means that the wave function of electrons in the He atom is

$$\Psi_{He} = \psi_{1s}(\vec{x}_1)\psi_{1s}(\vec{x}_2)\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$$

where, in the spinor $|\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle$, the first arrow is for m_{s1} and the second for m_{s2}.

There is a perhaps more intuitive approach to obtaining this same solution. It goes as follows. First, let us ignore spin. Let us simply put two electrons into the 1s level. What is a possible wave function? Clearly $\psi_{1s}(\vec{x}_1)\psi_{1s}(\vec{x}_2)$ will do. Note that this is a symmetric product with respect to exchange of coordinates $\vec{x}_1$ and $\vec{x}_2$. If electrons were bosons with spin 0, then this would be a good solution as is. But they are not. They are fermions with spin 1/2. Since the spatial wave function is symmetric, the only way to make the total wave function anti-symmetric is to make the spin wave function part to be anti-symmetric. With two spin halves, we know how to do it from the previous lecture! Just form the spin singlet state with total spin 0. This is how we can, perhaps, understand the above wave function.

Example 2.3. Vanadium Ion

Vanadium exists in various oxidation states, including V^{3+} corresponding to two electron in the 3d shell, giving rise to a non-zero total spin quantum number (see Example 3.1 below), which leads to magnetism. In this example, let us consider two 3d orbitals $\psi_{xy} \equiv |xy\rangle$ and $\psi_{yz} \equiv |yz\rangle$, for example. The subscripts xy and yz indicate the rotation symmetry of these orbitals. The only property that we will use about these orbitals is that they are orthogonal, so do not worry too much if you are not comfortable with these notations. Now suppose we ask the question what is the two body wave function for putting two electrons in ψ_{xy} and ψ_{yz} and both spins pointing up. The answer is

$$\begin{aligned}|\Psi_{11}\rangle &= \frac{1}{\sqrt{2}}\begin{vmatrix} |xy,\uparrow\rangle_1 & |yz,\uparrow\rangle_1 \\ |xy,\uparrow\rangle_2 & |yz,\uparrow\rangle_2 \end{vmatrix} \\ &= \frac{1}{\sqrt{2}}(|xy,yz,\uparrow\uparrow\rangle - |yz,xy,\uparrow\uparrow\rangle) \\ &= \frac{1}{\sqrt{2}}(|xy,yz\rangle - |yz,xy\rangle)|\uparrow\uparrow\rangle\end{aligned}$$

where the subscripts 1,2 mean coordinates 1,2, and $|xy,yz,\uparrow\uparrow\rangle = \psi_{xy}(\vec{x}_1)\psi_{yz}(\vec{x}_2)|\uparrow\uparrow\rangle$ etc. In this example, the spin part is nicely separated. Now, we say that the two spins are different. What is the wave function? Two possible Slater determinants are:

$$\frac{1}{\sqrt{2}}\begin{vmatrix} |xy,\uparrow\rangle_1 & |yz,\downarrow\rangle_1 \\ |xy,\uparrow\rangle_2 & |yz,\downarrow\rangle_2 \end{vmatrix}, \ \frac{1}{\sqrt{2}}\begin{vmatrix} |xy,\downarrow\rangle_1 & |yz,\uparrow\rangle_1 \\ |xy,\downarrow\rangle_2 & |yz,\uparrow\rangle_2 \end{vmatrix}$$

Without further information, all we can say is that the state is a linear combination of these two. If the total spin is a good quantum number, then we should form eigenstates of the total spin. Such states are easily formed by adding or subtracting these two states and normalizing the result.

$$\begin{aligned}|\Psi_{10}\rangle &= \frac{1}{2}(|xy,yz\rangle - |yz,xy\rangle)(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |\Psi_{00}\rangle &= \frac{1}{2}(|xy,yz\rangle + |yz,xy\rangle)(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)\end{aligned}$$

Note that $|\Psi_{10}\rangle$ could have been obtained from $|\Psi_{11}\rangle$ by applying $\hat{S}_- = \hat{S}_{1,-} + \hat{S}_{2,-}$ to it and normalizing the result. Now, it is obvious that the notation $|\Psi_{Sm}\rangle$ corresponds to the total spin S and its z component S_z. Finally,

$$|\Psi_{1-1}\rangle = \frac{1}{\sqrt{2}}(|xy,yz\rangle - |yz,xy\rangle)|\downarrow\downarrow\rangle$$

$|\Psi_{10}\rangle$ and $|\Psi_{00}\rangle$ illustrate the general property that a many body wave function for fermions is a linear superposition of Slater determinants.

Example 2.4. Two "Distinguishable Particles" and Bosons

For two one electron states ψ_a and ψ_b, the wave function for two "distinguishable particles" is

$$\Psi_D(1,2) = \psi_a(1)\psi_b(2) \ \text{ or } \ \psi_a(2)\psi_b(1)$$

For two bosons

$$\Psi_B(1,2) = A(\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1))$$

where A is a normalization constant (Bonus Homework).

3. Time-independent Perturbation Theory

Problems in real life are not easily solvable. The perturbation theory is an essential *practical* piece of Quantum Mechanics in this sense.

The concept of the perturbation theory is the following. Suppose one is given a Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{H}_1$$

where the Hamiltonian consists of an "easy part" $\hat{H}_0$ and a "difficult but small part" $\hat{H}_1$. Since the second part is small compared to the first part, one can proceed with the easy part first. We assume that one has obtained a complete set of eigenstates and eigenvalues for $\hat{H}_0$:

$$\hat{H}_0|n,0\rangle = E_{n,0}|n,0\rangle$$

where $E_{n,0}$ is by definition an increasing function of n. We consider those problems where n is an integer index. This does not necessary mean bound states only. In the theory of solids, a subset of continuum states reduced by the symmetry (crystal symmetry group) can be treated separately and they, while part of continuum states, form a discrete subset.

Having found the states $|n,0\rangle$, we can use them as our natural basis. So, we obtain the matrix representation,

$$\hat{H} = \begin{bmatrix} E_{0,0}+M_{00} & M_{01} & M_{02} & ... & ... & & \\ M_{10} & E_{1,0}+M_{11} & M_{12} & ... & .. & ... & \\ M_{20} & M_{21} & E_{2,0}+M_{22} & M_{23} & ... & & ... \\ ... & ... & M_{32} & E_{3,0}+M_{33} & ... & ... & \\ ... & ... & ... & ... & ... & & \\ & ... & & ... & & ... & \\ & & ... & & & & ... \end{bmatrix} \tag{3.1}$$

where,

$$M_{mn} = \langle m,0|\hat{H}_1|n,0\rangle \tag{3.2}$$

Since $M_{mn} = M^*_{nm}$, one can see that the matrix is Hermitian, as it should be. Suppose now, we are interested in some fixed but arbitrary value of n. The question that we ask is, "how does E_n change due to $\hat{H}_1$?". For this question to make sense[3], we make the following assumption

$$\Delta_{n,0} \gg M \tag{3.3}$$

$$\Delta_{n,0} \equiv \min(|E_{n,0} - E_{n\pm1,0}|) \tag{3.4}$$

$$M = \max(|M_{ml}|) \tag{3.5}$$

This is the condition in which the perturbation theory can give the answer as to how E_n is modified due to $\hat{H}_1$ and what the corresponding eigenstate is, to any accuracy desired.

3.1. **Non-Degenerate Perturbation.** The non-degenerate perturbation theory is, in a way, *the* perturbation theory, as you will see below what we need to do in the case of the so-called "degenerate" perturbation theory. The pre-requisite for the non-degenerate perturbation theory is just Eq. 3.3. In this case, the exact eigenstate can be "followed" from the unperturbed state $|n\rangle_0$ with the same label n:

$$|n\rangle = |n,0\rangle + |n,pc\rangle = |n,0\rangle + |n,1\rangle + |n,2\rangle + |n,3\rangle + ... \tag{3.6}$$

where the index i after n in $|n,i\rangle$ means that that term is smaller than the previous term by a factor of $M/\Delta_{n,0} \ll 1$. Equivalently, you can think of $\hat{H}_1$ as being proportional to a small parameter λ, so that $|n,i\rangle$ is proportional to λ^i. pc means *p*erturbation *c*orrection. The full equation to solve is

$$\left[\hat{H}_0 + \hat{H}_1\right]|n\rangle = E_n|n\rangle \tag{3.7}$$

where E_n can be rewritten as

$$E_n = E_{n,0} + E_{n,pc} = E_{n,0} + E_{n,1} + E_{n,2} + E_{n,3} + ... \tag{3.8}$$

in the same notation as above. Eq. 3.7 can be re-arranged trivially to give

$$\left[\hat{H}_0 - E_{n,0}\right]|n\rangle = \left[E_{n,pc} - \hat{H}_1\right]|n\rangle \tag{3.9}$$

Apply $\langle n,0|$ from the left hand side, and we get 0, since $\langle n,0|\left[\hat{H}_0 - E_{n,0}\right] = \langle n,0|\left[E_{n,0} - E_{n,0}\right] = 0$ and so we get an important condition

$$\langle n,0|\left[E_{n,pc} - \hat{H}_1\right]|n\rangle = 0 \tag{3.10}$$

Use $|n\rangle = |n,0\rangle + |n,pc\rangle$ on the left hand side of Eq. 3.9, and we notice again that $|n,0\rangle$ will be annihilated by $\hat{H}_0 - E_{n,0}$. After that, we introduce a constant δ in this way:

$$\left[\hat{H}_0 - E_{n,0} + \delta\right]|n,pc\rangle = \left[E_{n,pc} - \hat{H}_1\right]|n\rangle$$

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[3] The assumptions made here make it trivially possible to "track" the quantum number n, before and after the "turning on" of $\hat{H}_1$, since the change of E_n due to $\hat{H}_1$ is much smaller than the original level spacings around E_n. You can consider this as an elementary example of the more general adiabatic theorem (Chapter 10 of Griffiths).

We introduce δ since $\hat{H}_0 - E_{n,0}$ is a diagonal matrix (see Eq. 3.1) with one diagonal element 0. Thus, it is not invertible. However, we will soon see that this is not a problem. For now, we assume that a suitably chosen δ makes all diagonal elements non-zero, possible since all E_n values are distinct, and thus makes $\hat{H}_0 - E_{n,0} + \delta$ invertible. So, we invert it and get

$$|n, pc\rangle = \frac{1}{\hat{H}_0 - E_{n,0} + \delta}\left[E_{n,pc} - \hat{H}_1\right]|n\rangle$$

Now, we insert the resolutions of identity $\sum_m |m,0\rangle\langle m,0| = 1$ into the right hand side and obtain:

$$\begin{aligned} |n, pc\rangle &= \frac{1}{\hat{H}_0 - E_{n,0} + \delta}\sum_m |m,0\rangle\langle m,0|\left[E_{n,pc} - \hat{H}_1\right]|n\rangle \\ &= \sum_m |m,0\rangle\frac{\langle m,0|\left[E_{n,pc} - \hat{H}_1\right]|n\rangle}{E_{m,0} - E_{n,0} + \delta} \end{aligned}$$

But, we see from Eq. 3.10 that the m sum actually does not include n. So, we can take $\delta \to 0$ without any trouble[4]:

$$|n, pc\rangle = \sum_{m\neq n}\frac{|m,0\rangle\langle m,0|\left[E_{n,pc} - \hat{H}_1\right]|n\rangle}{E_{m,0} - E_{n,0}} \tag{3.11}$$

Since $|n, pc\rangle$ does not include $|n,0\rangle$, $\langle n,0|n,pc\rangle = 0$, which means, from Eq. 3.6,

$$\langle n,0|n\rangle = 1 \tag{3.12}$$

Using this in Eq. 3.10, we get

$$E_{n,pc} = \langle n,0|\hat{H}_1|n\rangle \tag{3.13}$$

These last three equations form *the complete formal solutions* for the non-degenerate time-independent perturbation theory. The first (Eq. 3.11) gives the perturbation correction to the stationary state, the second (Eq. 3.12) the normalization convention and the third (Eq. 3.13) the perturbation correction to the energy eigenvalue. Note that the normalization convention is *not* $\langle n|n\rangle = 1$. Within the perturbation theory, it is the most convenient to postpone the more correct normalization procedure and use the approximate normalization convention, Eq. 3.12. The correct normalization $\langle n|n\rangle = 1$ can and should be imposed *after* the perturbation solution has been settled, when it is required by other projects to be built on the perturbation solutions.

There is one important thing to note from the eigenvalue equation, Eq. 3.13: the i-th order correction in $|n\rangle$ gives the $i+1$-th order correction in E_n, since $\hat{H}_1 \sim M$ by definition. So, using a basic iterative method, the formal solutions Eqs. 3.11 and 3.13 can be used to any accuracy desired. Let us work out the first two approximate solutions for eigenvalues. First, the zero-th order solution for the ket is

$$|n\rangle \approx |n,0\rangle \tag{3.14}$$

which leads to the first order solution for the energy correction

$$E_{n,1} = \langle n,0|\hat{H}_1|n,0\rangle = M_{nn} \tag{3.15}$$

Plugging these two results in the RHS of Eq. 3.11, we get the first order correction to the ket

$$\begin{aligned} |n,1\rangle &= \sum_{m\neq n}|m,0\rangle\frac{M_{nn}\delta_{mn} - M_{mn}}{E_{m,0} - E_{n,0}} \\ (m \neq n \text{ means } \delta_{mn} = 0) &= -\sum_{m\neq n}\frac{|m,0\rangle\langle m,0|\hat{H}_1|n,0\rangle}{E_{m,0} - E_{n,0}} \end{aligned} \tag{3.16}$$

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[4] The reason to have introduced δ is just for the clarity of the presentation. We could have said that the inverse of $\hat{H}_0 - E_{n,0}$ is well-defined in the sub-space spanned by $\{|m,0\rangle | m \neq n\}$, and could have justified the inversion within this subspace.

Plugging this into Eq. 3.13, we now get the 2nd order correction in energy

$$E_{n,2} = -\sum_{m \neq n} \frac{\left|\langle m, 0|\hat{H}_1|n, 0\rangle\right|^2}{E_{m,0} - E_{n,0}} \tag{3.17}$$

You can see that this iteration can go on indefinitely and give you corrections in increasing powers of M, as it is necessary. For the purpose of this note, we will stop here. Eqs. 3.15 and 3.17 are *very* valuable in practice.

It is important to note that the 2nd order energy correction always lowers the ground state (say $n = 0$), since for the ground state $E_{m,0} - E_{0,0} > 0$ for any $m \neq 0$.

Example 3.1. Exchange Interaction

Suppose there are two electrons in two states, ψ_a and ψ_b, that are orthogonal to each other. Which total spin of the two electrons, 1 or 0, would be more energetically favorable? If the total spin is 1, then the spin wave function part is symmetric and so the total wave function is

$$\Psi_{S=1} = \frac{1}{\sqrt{2}} \left(\psi_a(\vec{x}_1)\psi_b(\vec{x}_2) - \psi_b(\vec{x}_1)\psi_a(\vec{x}_2)\right) |S = 1, m_s\rangle$$

while if the total spin is 0

$$\Psi_{S=0} = \frac{1}{\sqrt{2}} \left(\psi_a(\vec{x}_1)\psi_b(\vec{x}_2) + \psi_b(\vec{x}_1)\psi_a(\vec{x}_2)\right) |S = 0, m_s\rangle$$

(Exercise: verify the normalization factor $1/\sqrt{2}$, using the probability sum rule.)

Note that, when $\vec{x}_1 = \vec{x}_2$, $\Psi_{S=1} = 0$ while $\Psi_{S=0} \neq 0$. What this means is that the two electrons can occupy the same position in the case of $S = 0$ due to the spin part taking care of the wave function anti-symmetry, while for $S = 1$ this is not allowed. The antisymmetric nature of the spatial wave function means that the two particles are farther away. Qualitatively, researchers came to describe this situation by saying that two electrons with equal spins tend to avoid each other due to statistics. It is as though an electron carries with it a "hole" in which another electron with the same spin is disallowed to enter or is repelled from. This is the concept of *the Slater exchange hole*[5].

So far, we have not come to the real reason why $\Psi_{S=1}$ and $\Psi_{S=0}$ differ in energy. To start with, let us take the Hamiltonian as

$$\begin{aligned} \hat{H} &= \hat{H}_1 + \hat{H}_2 \\ \hat{H}_1 &= -\frac{\hbar^2}{2m_1}\nabla_1^2 + V(\vec{x}_1) \\ \hat{H}_2 &= -\frac{\hbar^2}{2m_2}\nabla_2^2 + V(\vec{x}_2) \end{aligned}$$

Let us assume, without loss of generality, that ψ_a and ψ_b are stationary states with respective <u>energies</u> E_a, E_b:

$$\begin{aligned} \hat{H}_i\psi_a(\vec{x}_i) &= E_a\psi_a(\vec{x}_i) \\ \hat{H}_i\psi_b(\vec{x}_i) &= E_b\psi_b(\vec{x}_i) \end{aligned}$$

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[5] This is equivalent to the concept of "exchange force" described in Section 5.1.2 of Griffiths. In my opinion the term "exchange force" is to be avoided, since there is really no force. Also, the real effect of the exchange statistics is the "exchange interaction" described here. I advise caution in reading Section 5.1.2 of Griffiths.

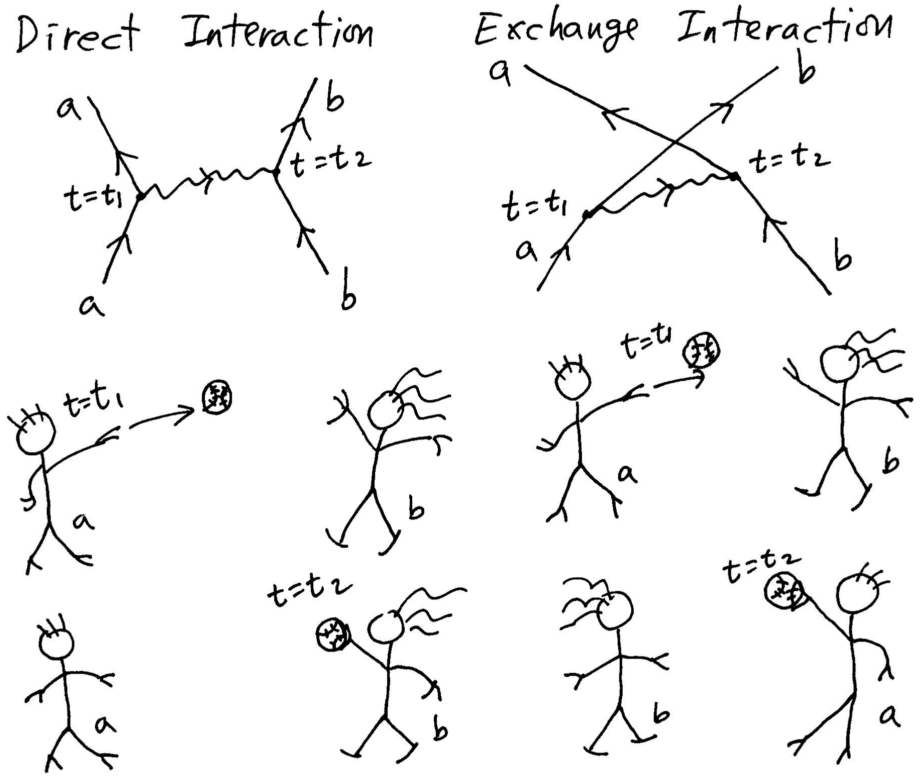

Figure 3.1. *Direction Interaction and Exchange Interaction.* The above diagrams (Feynman diagrams) and cartoons illustrate the direct interaction and the exchange interaction. In both cases, Abe (electron) throws a ball (photon) to Bella (electron) at $t = t_1$. In the direct interaction case, Bella catches the ball at $t = t_2$ and that is how they interact. In the exchange interaction case, Abe and Bella swiftly exchange their places, and Abe catches the ball that he threw. Well, this "swiftly exchanging places" actually never occurs. In Quantum Mechanics, there is no need for "swiftly exchanging places" because, simply, Abe=Bella (identical particles). For two Classical objects exchanging photons, they cannot ever beat photons, and so the exchange interaction is simply impossible. Due to the identical nature of fundamental particles, the exchange interaction occurs in Quantum Mechanics, but there is no such thing in Classical Mechanics. Another aspect of the exchange interaction is that when the interaction is spin independent, like Coulomb interaction, the spin quantum number of the two electrons must be the same for it to occur, because the fermion line in the above Feynman diagrams cannot change spin.

where $i = 1, 2$. Then,

$$\begin{aligned}
\hat{H}\Psi_{S=1} &= \frac{1}{\sqrt{2}}|S=1, m_s\rangle \left[\hat{H}_1 + \hat{H}_2\right] (\psi_a(\vec{x}_1)\psi_b(\vec{x}_2) - \psi_b(\vec{x}_1)\psi_a(\vec{x}_2)) \\
(\text{Applying } \hat{H}_1) &= \frac{1}{\sqrt{2}}|S=1, m_s\rangle [E_a\psi_a(\vec{x}_1)\psi_b(\vec{x}_2) - E_b\psi_b(\vec{x}_1)\psi_a(\vec{x}_2) + \\
(\text{Applying } \hat{H}_2) & \quad E_b\psi_a(\vec{x}_1)\psi_b(\vec{x}_2) - E_a\psi_b(\vec{x}_1)\psi_a(\vec{x}_2)] \\
&= (E_a + E_b)\Psi_{S=1} \\
\hat{H}\Psi_{S=0} &= (E_a + E_b)\Psi_{S=0} \, (\text{similarly})
\end{aligned}$$

So, these two states have *identical energies.* However, so far, our model has been crude. In reality, when one brings two electrons together, there is bound to be a strong repulsive interaction. This interaction is significant, on the order of a few eV, so it should be included. Thus, consider the Coulomb energy term

$$\hat{H}_1 = V(\vec{x}_1, \vec{x}_2)$$

with the symmetry $V(\vec{x}_1, \vec{x}_2) = V(\vec{x}_2, \vec{x}_1)$. To get a sense of the effect of this term, let us apply the first order perturbation theory. The first order energy correction for the $S = 1$ state is (with a short-hand notation $1, 2$ for $\vec{x}_1, \vec{x}_2$ respectively)

$$\begin{aligned} E_{S=1,1} &= \frac{1}{2}\int d\vec{x}_1 d\vec{x}_2 \left(\psi^*_{a,1}\psi^*_{b,2} - \psi^*_{b,1}\psi^*_{a,2}\right) V(1,2) \left(\psi_{a,1}\psi_{b,2} - \psi_{b,1}\psi_{a,2}\right) \\ \text{(using } V(1,2) = V(2,1)\text{)} &= \int d\vec{x}_1 d\vec{x}_2 |\psi_{a,1}|^2 V(1,2) |\psi_{b,2}|^2 - \int d\vec{x}_1 d\vec{x}_2 \psi^*_{a,1}\psi_{b,1} V(1,2) \psi^*_{b,2}\psi_{a,2} \\ &= D - E \\ E_{S=0,1} &= D + E \quad \text{(similarly)} \end{aligned}$$

The integral D is the direct Coulomb interaction, while E is the exchange Coulomb interaction, or the *exchange interaction*. E arises due to the identical nature of the two electrons, and it has no Classical analogue. These two terms are graphically represented in Figure 3.1. Note that both D and E are positive numbers for Hydrogen orbitals, and also in general. As a result, the spin triplet state is always lower in energy. One can intuitively understand this from the Slater exchange hole concept. Since electrons with the same spin have less probability to be in the proximity to each other, the net Coulomb repulsion is less.

The exchange interaction explains is the basis for Hund's rule (see the next section), which is the most dramatically realized in transition metal ions, such as Mn^{2+} (3d^5) and Fe^{2+} (3d^6). The first Hund's rule is that the spin angular momentum is maximized. This is because, by doing so, the lowering of the exchange interaction in the 3d shell is optimized. So, the total spin quantum number for Mn^{2+} (3d^5) is $S = 5/2$ while that for Fe^{2+} (3d^6) is $S = 2$.

Definition 3.2. Spectroscopic Notation for Multiplet Terms and Hund's rule

In Atomic Physics, spectroscopic notation for various angular momentum states ("multiplets") has been developed from early days of QM, and there exists a standard one: ${}^{2S+1}L_J$, where S is the total spin, L is the total orbital angular momentum, and J is the total angular momentum (i.e. sum of $\hat{\vec{L}}$ and $\hat{\vec{S}}$). Table 5.1 of Griffiths can be read with this in mind. Hund's rule, justified by the exchange interaction and the spin orbit interaction, is a good guide to how those values of L, S, and J arise. Take C as an example: $(\text{He})(2s)^2(2p)^2$. Here, we take it as given that the "accidental degeneracy" of the Hydrogen problem is removed and so energy is dependent on both n and l, as commented in a previous lecture, and also discussed below (Note 3.5). Completely closed shells such as (He) and $(2s)^2$ do not contribute any angular momentum at all (Exercise: prove this by using the Slater determinant), and so only the "unfilled shell" such as $(2p)^2$ cointributes, where an "unfilled shell" means that degenerate energy levels, such as six $2p$ orbitals, are not fully occupied. (i) Hund's first rule is that S is maximized. With two spins, this means $S = 1$. (ii) Hund's second rule is that L is maximized under the contraint of the first rule. With two spins parallel as in $S = 1$, the best the two electrons can do in terms of the orbital angular momentum is to occupy $l = 1$ and $l = 0$. This means $L = 1 + 0 = 1$, and so we have a P state. ($L = 0, 1, 2, 3, ...$ is called S, P, D, F for the total angular momentum, using capital letters.) (iii) Hund's third rule is that $J = |L - S|$ if the shell is less than half-full, $J = L + S$ otherwise. $(2p)^2$ is less than half full, since $2p$ has the degeneracy of 6. This means $J = 1 - 1 = 0$ for carbon. Thus, $S = 1$, $L = 1$ (P), and $J = 0$, we arrive at the multiplet term notation

$${}^3P_0$$

for C.

The three rules listed above may be collectively referred to as "Hund's rule," which works quite well in general. However, it can, and does, break down, for instance in Co or U compounds.

Example 3.3. Fine Structure of Atoms

Two things contribute to the fine structure of atoms. One is the relativistic correction and the other is the spin-orbit interaction. The relativistic correction is due to the energy

$$\begin{aligned} E &= \sqrt{m^2c^4 + p^2c^2} \\ &= mc^2\left[1 + \frac{p^2}{m^2c^2}\right]^{1/2} \\ &= mc^2\left[1 + \frac{1}{2}\frac{p^2}{m^2c^2} + \frac{1}{2}\frac{1}{2}\left(-\frac{1}{2}\right)\frac{p^4}{m^4c^4} + ...\right] \\ &\approx mc^2 + \frac{p^2}{2m} - \frac{1}{8}\frac{p^4}{m^3c^2} \end{aligned}$$

For the energy level of the Hydrogen problem, the first order energy correction is

$$E_{n,1,rel} = -\frac{1}{8m^3c^2}\langle nl|\hat{p}^4|nl\rangle$$

The calculation is a bit involved. Here, we just state the answer (see Griffiths for steps),

$$E_{n,1,rel} = -\frac{E_n^2}{2mc^2}\left[\frac{4n}{l+1/2} - 3\right] \tag{3.18}$$

Note that $E_n = -\frac{mc^2\alpha^2}{2}\frac{1}{n^2}$, and so the fine structure correction is $\sim E_n\alpha^2$, which is why the fine structure constant is called that.

Another fine structure effect is the spin orbit interaction which is given by (Eq. 6.61 of Griffiths)

$$\hat{H}'_{so} = \frac{e^2}{8\pi\epsilon_0}\frac{1}{m^2c^2r^3}\hat{\vec{L}}\cdot\hat{\vec{S}}$$

As discussed in the previous lecture, this Hamiltonian does not commute with $\hat{L}_z$ or $\hat{S}_z$. It does commute with $\hat{J}^2, \hat{J}_z, \hat{L}^2, \hat{S}^2$, and good quantum numbers are jm_jls. Note that $2\hat{\vec{L}}\cdot\hat{\vec{S}} = j(j+1) - l(l+1) - s(s+1)$, when evaluated on ket $|jm_jls\rangle$. The radial integral is a bit involved again, and the result is

$$E_{n,1,so} = \frac{E_n^2}{2mc^2}\left[\frac{4n}{l+1/2} - \frac{4n}{j+1/2}\right]$$

which is of the same order as $E_{n,1,rel}$! The total fine structure correction to the Hydrogen energy is

$$E_{n,1,fs} = \frac{E_n^2}{2mc^2}\left[3 - \frac{4n}{j+1/2}\right] = E_n\frac{\alpha^2}{n^2}\left[\frac{3}{4} - \frac{n}{j+1/2}\right]$$

Note 3.4. ***Wave Function for the Fine Structure Problem***

Above, we applied the first order perturbation in energy, which means that the wave function did not change. For the Hydrogen problem with Coulomb potential only, we can take the stationary state wave function to be be $|nlm_lm_s\rangle$ or $|nljm_j\rangle$. Due to the spin orbit interaction, the wave function for the fine structure problem *has to* be chosen as $|nljm_j\rangle$. Notice that there is a degeneracy of $2j+1$ for each of the states $|nljm_j\rangle$ with different m_j values. Above, we acted as though that this degeneracy does not matter, although the theory was developed specifically for the non-degenerate case. This is fine, because the symmetry of the perturbing Hamiltonian is such that $\langle jm_j|\hat{H}_{fs}|jm_j'\rangle = 0$ if $m_j \neq m_j'$.

Note 3.5. ***Spin-Orbit Splitting and Its Magnitude***

The fact that the fine structure perturbation lifts the accidental degeneracy is little importance in real atoms, since there the accidental degeneracy is lifted by the energy scale that is an order of magnitude larger – Coulomb interaction between electrons. However, what is important about the fine structure effect is that it splits an l level to two j levels, since the stationary state wave function is now unambiguously $|nljm_j\rangle$ and the energy is dependent on j. This splitting is called the *spin-orbit splitting*, as it $(-E_n\frac{\alpha^2}{n}\frac{1}{j+1/2}$ in the above equation) comes from the spin orbit interaction alone[6]. For instance, the 2p level (n=2, l=2) splits into $2p_{3/2}$ and $2p_{1/2}$ levels. $2p_{1/2}$ has a lower energy than $2p_{3/2}$, by $\sim \alpha^2 E_n$. In real materials, the Coulomb potential has to be multiplied by the atomic number Z, and this results in[7] $E_n \to Z^2 E_n$ and $E_{fs} \to Z^4 E_{fs}$. So, there is a larger spin orbit splitting for an atom with a larger Z value. The point in case: for 2p orbitals of the Hydrogen orbital, the spin orbit splitting calculated here is $E_2\alpha^2/4 = 3.3 \times 10^{-6}$ eV, which is quite small, while for 2p levels of transition metal atoms (Mn, Fe, etc.), the spin orbit splitting for 2p is on the order of 10 eV! For various reasons, the spin orbit interaction in the valence shell is of high current interest. That is typically small, on the order of a few tens of 10 meV, while for some states on a specially prepared solid surface a splitting as large as 1 eV has been claimed.

3.2. **"Degenerate" Perturbation Theory.** Some problems tend to have degenerate energy levels for $\hat{H}_0$. These actually tend to be physically interesting cases. Suppose, again, that we are interested in obtaining the perturbation solution for $|n\rangle$. By degenerate energy levels, we mean there are some m values for which $E_{m,0} = E_{n,0}$. Actually this condition is not quite realistic enough. What we need to include are those levels whose energies are sufficiently close to $E_{n,0}$ compared with M, defined in Eq. 3.5. So, we define a set of of such kets

$$B_n = \{|m,0\rangle \mid |E_{m,0} - E_{n,0}| \lesssim M\}$$

and also define

$$I_n = \{m \mid |m,0\rangle \in B_n\}$$

We assume the the number of elements in I_n and B_n is finite. Consider the linear space $\mathcal{V}_n$ spanned by B_n. For now, we can forget about those m values outside I_n and can happily and readily (using computer, if necessary) diagonalize the following finite-dimensional Hamiltonian *sub*-matrix

$$h_{ij} = \langle i,0|\hat{H}|j,0\rangle,\ i,j \in I_n$$

After the diagonalization is done, we will have found a new orthonormal basis that span $\mathcal{V}_n$, and we call them

$$B_n^{(s)} = \{|m^{(s)},0\rangle \mid m \in I_n\}$$

$$\langle l^{(s)},0|\hat{H}|m^{(s)},0\rangle = \delta_{lm} E_{l,0}^{(s)}$$

Now, the total Hamiltonian looks like the following, where, just as an example, we assume that $I_n = \{1,2,3\}$:

$$\hat{H} = \begin{bmatrix} E_{0,0}+M_{00} & M_{01} & M_{02} & M_{03} & M_{04} & \cdots & \\ M_{10} & E_{1,0}^{(s)} & 0 & 0 & M_{14} & \cdots & \cdots \\ M_{20} & 0 & E_{2,0}^{(s)} & 0 & M_{24} & \cdots & \\ M_{30} & 0 & 0 & E_{3,0}^{(s)} & M_{34} & \cdots & \cdots \\ M_{40} & M_{41} & M_{42} & M_{43} & E_{4,0}+M_{44} & \cdots & \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \\ & \cdots & & \cdots & & & \cdots \end{bmatrix}$$

Since the basis changed partially, we need to clean up the notation. We use $0'$ to denote the entire, partially new, basis set. That is,

$$|l,0'\rangle = |l^{(s)},0\rangle \text{ if } l \in I_n,\ |l,0\rangle \text{ otherwise}$$

$$E_{l,0'} = E_{l,0}^{(s)} \text{ if } l \in I_n,\ E_{l,0} \text{ otherwise}$$

---

[6] However, the absolute position is dependent on both relativistic effect and spin orbit interaction. In the literature, when expressions "relativistic correction" and "spin orbit correction" are used, it should be understood that one automatically implies the other and vice versa.

[7] This effect is exaggerated for valence electrons in the outermost shell, since they do not see the "bare" nucleus charge most of the time as the nucleus charge screened/compensated by negative charge of electrons in inner shells. So, the effect of Z gets reduced on going from inner shells (e.g. 1s) to valence shells.

Namely, the above matrix is represented by the $|l,0'\rangle$ basis. Note that M_{lm} in this matrix representation is given by

$$M_{lm} = \langle l,0'|\hat{H}|m,0'\rangle = \langle l,0'|\hat{H}_1|m,0'\rangle$$

This is because M_{lm} is finite only when at least one of l,m is outside of I_n. In that case, either the bra or the ket is an eigenstate of $\hat{H}_0$ and thus $\langle l,0'|\hat{H}_0|m,0'\rangle = 0$. One has to be careful, though, not to over-interpret this equality. I.e., it should not be interpreted backwards, going from $\hat{H}_1$ to M_{lm}. When both l,m are inside I_n, $\hat{H}_1$ generally has finite matrix elements, which do not appear in M_{lm}, since they are already taken care of by the diagonalization of the sub-matrix.

It makes sense to divide the Hamiltonian into

$$\hat{H} = \hat{H}'_0 + \hat{H}'_1$$

where

$$\begin{aligned}\hat{H}'_0 &= \text{diagonal matrix with its elements } E_{l,0'} = E_{l,0} \text{ or } E^{(s)}_{l,0} \\ \hat{H}'_1 &= \text{matrix with elements } M_{lm}\end{aligned}$$

By definition, then,

$$\hat{H}'_0|m,0'\rangle = E_{n,0'}|m,0'\rangle$$

Also, from the above discussin, it is clear that $\hat{H}'_1$ and $\hat{H}_1$ have the same matrix elements if at least one of l,m is outside I_n,

$$\langle l,0'|\hat{H}'_1|m,0'\rangle = \langle l,0'|\hat{H}_1|m,0'\rangle = M_{lm}$$

but, within $\mathcal{V}_n$, $\hat{H}'_1 = 0$ while $\hat{H}_1 \neq 0$.

Now we can proceed exactly like in the non-degenerate case assuming[8] that $\Delta_{n,0'} \gg M$. The ket is

$$|n\rangle = |n^{(s)},0\rangle + |n,pc\rangle$$

and the energy is

$$E_n = E'_{n,0} + E_{n,pc} = E^{(s)}_{n,0} + E_{n,pc}$$

The solution corresponding to Eq. 3.11 is

$$|n,pc\rangle = \sum_{m\neq n} \frac{|m,0'\rangle\langle m,0'|\left[E_{n,pc} - \hat{H}'_1\right]|n\rangle}{E_{m,0'} - E^{(s)}_{n,0}} \tag{3.19}$$

The eigenvalue correction is

$$E_{n,pc} = \langle n^{(s)},0|\hat{H}'_1|n\rangle \tag{3.20}$$

and the normalization convention is

$$\langle n^{(s)},0|n\rangle = 1 \tag{3.21}$$

Note that $\langle n^{(s)},0|\hat{H}'_1|n^{(s)},0\rangle = 0$. *The first order correction in energy (and the zeroth order wave function) has already been included in the solutions* $E^{(s)}_{n,0}$ *(and* $|n^{(s)},0\rangle$*).*

The first order correction for the wave function is

$$\begin{aligned}|n,1\rangle &= -\sum_{m\neq n} \frac{|m,0'\rangle M_{mn}}{E_{m,0'} - E^{(s)}_{n,0}} \\ &= -\sum_{m\notin I_n} \frac{|m,0\rangle\langle m,0|\hat{H}_1|n^{(s)},0\rangle}{E_{m,0} - E^{(s)}_{n,0}} \qquad (3.22)\end{aligned}$$

---

[8] Nobody can guarantee that this condition will come true! If the problem is such that it does not come true, do not despair. We can include one more m adjacent to $\min(I_n)$ or $\max(I_n)$ and then re-diagonalize h_{ij}, which is now one dimension larger than before. We can keep doing this until we make sure that $\Delta_{n,0'} \gg M$ come true. It is likely to come true, although there is no general theorem that it should.

The 2nd order correction in energy is

$$E_{n,2} = -\sum_{m \notin I_n} \frac{\left|\langle m,0|\hat{H}_1|n^{(s)},0\rangle\right|^2}{E_{m,0} - E^{(s)}_{n,0}} \tag{3.23}$$

The summation for higher order corrections are not going to be limited to $m \notin I_n$. The summation in Eq. 3.19 *cannot* be replaced by $\sum_{m \notin I_n}$, because $|n\rangle$ can overlap with $|j,0\rangle$ and $\hat{H}_1'$ can then couple $|j,0\rangle$ to $\langle m,0|$ where $m \in I_n$. So, as the perturbation expansion goes beyond the 2nd order in energy, all $m \neq n$ values will make contributions.

Example 3.6. ***Two "Well" Problem Redux – LCAO and MASER***

We have considered two finite wells before. This case can be considered within the perturbation theory if the two wells are not too close to each other.

In this example, we will assume that there are two identically shaped potentials $V_1 = V(x+b)$ and $V_2 = V(b-x)$, symmetrically positioned[9] at $\mp b$. We take the "well" potential $V(x)$ to be a rather unrestricted potential, with the only condition being that it is an overall negative-valued potential vanishing as $|x| \to \infty$. This assumption insures that there is a bound ground state at a negative energy. The total Hamiltonian is

$$\hat{H} = \hat{T} + \hat{V}_1 + \hat{V}_2$$

We will be interested in the ground state of $\hat{H}$. We will only consider a large enough b so that all perturbation energy scales that we encounter (β, t below) are much smaller than the energy separation between the ground state and the first excited state. Thus, it suffices to focus on the ground state of the potential $V(x)$,

$$\left[\hat{T} + \hat{V}\right] \psi_G(x) = E_G \psi_G(x)$$

Let us assign $|1\rangle = \psi_G(x+b)$ and $|2\rangle = \psi_G(b-x)$. Then,

$$\left[\hat{T} + \hat{V}_i\right] |i\rangle = E_G|i\rangle \text{ for } i = 1,2$$

Note that $|1\rangle$ and $|2\rangle$ are *not* orthogonal in general. We define

$$\alpha \equiv \langle 1|2\rangle$$

Note that

$$\hat{H}|1\rangle = E_G|1\rangle + \hat{V}_2|1\rangle \tag{3.24}$$

$$\hat{H}|2\rangle = E_G|2\rangle + \hat{V}_1|2\rangle \tag{3.25}$$

We define

$$\beta \equiv \langle 1|\hat{V}_2|1\rangle \tag{3.26}$$

$$t \equiv \langle 1|\hat{H}|2\rangle \tag{3.27}$$

The assumptions necessary for the perturbation theory is that $\alpha E_G, \beta, t \ll$ energy separation for the single well problem. Note that $\beta = \langle 2|\hat{V}_1|2\rangle$ also, since $\int dx |\psi_G(x+b)|^2 V(b-x) = \int dx |\psi_G(b-x)|^2 V(x+b)$ by change of variable. Before setting up the Hamiltonian matrix, it is better to define an orthonormal basis. Such basis is easy to set up:

$$|1'\rangle = |1\rangle,\ |2'\rangle = \left[|2\rangle - \alpha|1\rangle\right] / \sqrt{1 - |\alpha|^2}$$

---

[9] The reason to define $V_2 = V(b-x)$ is because the well itself may not be symmetric, i.e. we take the potential to be general so that $V(x)$ may, or may not, be equal to $V(-x)$.

will do. The matrix elements of $\hat{H}$ using this basis are complicated in general, but our purpose here is to keep track of the first leading order effect, and it suffices to keep terms linear in $\alpha E_G, \beta, t$. So,

$$\begin{aligned}\langle 1'|\hat{H}|1'\rangle &= E_G+\beta\\ \langle 2'|\hat{H}|2'\rangle &\approx E_G+\beta\\ \langle 1'|\hat{H}|2'\rangle &\approx t\end{aligned}$$

and

$$\hat{H}\approx\left[\begin{array}{cc} E_G+\beta & t\\ t^* & E_G+\beta\end{array}\right]$$

Here, we have a degenerate problem where the two levels $|1'\rangle=|1\rangle$ and $|2'\rangle\approx|2\rangle$ are closer together in energy than the perturbation terms such as t and β. Thus, diagonalizing this matrix, we get the first order correction to the energy, and the zeroth order wave function. The diagonalization is trivial and the two energies are

$$\begin{aligned}E_L &= E_G+\beta-|t|\\ E_H &= E_G+\beta+|t|\end{aligned}$$

where the subscripts L and H stand for "low" and "high" respectively. The corresponding wave functions are, assuming $t=|t|e^{i\theta}$,

$$\begin{aligned}|L\rangle &= \frac{1}{\sqrt{2}}\left[|1'\rangle-e^{-i\theta}|2'\rangle\right]\approx\frac{1}{\sqrt{2}}\left[|1\rangle-e^{-i\theta}|2\rangle\right]\\ |H\rangle &= \frac{1}{\sqrt{2}}\left[|1'\rangle+e^{i\theta}|2'\rangle\right]\approx\frac{1}{\sqrt{2}}\left[|1\rangle+e^{i\theta}|2\rangle\right]\end{aligned}$$

Notice how t plays the central role here. t is called[10] "hopping amplitude" or "tunneling amplitude" or "hybridization matrix element." Note that t is usually a real number. In fact, for all practical purposes[11], we can see that $t<0$, as follows. First note that from Eqs. 3.25 and 3.27

$$t=E_G\alpha+\langle 1|\hat{V}_1|2\rangle \tag{3.28}$$

When the wells are far from each other say compared to the width of the well, then the first term $E_G\alpha$ is dominant over the second term $\langle 1|\hat{V}_1|2\rangle$. In any case, for ordinary cases when wave functions are real and symmetric, both terms are negative numbers, and so $t<0$. Assuming this is the case, $\theta=\pi$, and thus

$$\begin{aligned}|B\rangle\equiv|L\rangle &\approx \frac{1}{\sqrt{2}}\left[|1\rangle+|2\rangle\right]\\ |A\rangle\equiv|H\rangle &\approx \frac{1}{\sqrt{2}}\left[|1\rangle-|2\rangle\right]\end{aligned}$$

where the notations B, A mean "bonding" and "anti-bonding" respectively.

While the problem has been treated as a one dimensional one so far, it is trivially extended to the case when the potential is a Coulomb potential in three dimensions. For instance, for H_2, $|1\rangle$ and $|2\rangle$ are 1s orbitals at the two proton sites. In this view, the method outlined here is the so-called linear combination of atomic orbitals (LCAO) model for the covalent bonding. We will continue to use the H_2 molecule as our example, while with some modifications of detail this example can be extended to other molecules without any qualitative change. The basic picture is that two 1s orbitals at the two hydrogen atoms are degenerate, and they "hybridize" with each other through the tunneling process, by t. As the result, two 1s orbitals form a bonding orbital $|B\rangle$ and an anti-bonding orbital $|A\rangle$. The bonding orbital has a higher probability density for the electron to be between two protons. In this case, the wave function is symmetric. The symmetric wave function

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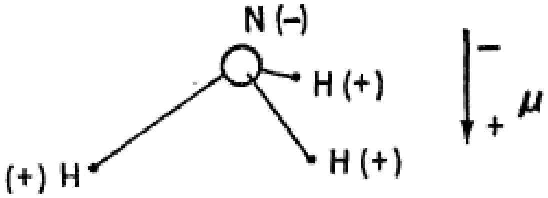
[10] Griffiths associates "exchange force" with t, in Section 5.1.2. It may be the best to avoid the term "exchange force." See Example 3.1 of this note for the more standard treatment of the exchange effect, i.e. the "exchange interaction."

[11] This is not a rule written in stone. In solids, it is suggested that t can change sign with some interesting consequences.

means that the kinetic energy is lowered (part of $E_G\alpha$ Eq. 3.28), the mechanism that always exists, while there can be some potential energy lowering as well. Since there is a spin degeneracy of 2 for electrons, one can put two electrons in the bonding orbital, which is an energetically favorable situation. This covalent bonding picture is usually described as follows[12]: (1) each atom gives up one electron, (2) the two atoms thus released stay in between the two atoms, shared by the two atoms, and (3) this sharing optimizes the energy lowering for the bonding to occur. Step (1) is possible only between atoms which are "like each other" in the electro-negativity sense, for instance between Hydrogen atoms in H_2, Si atoms in the Si crystal, C atoms in all C allotropes, and between Ga (In,Zn) and As (S,Se) in various semiconductors like GaAs, InAs, ZnSe, ZnS, etc. Since the two electrons occupy the same orbitals, the spins must be opposite to each other, and this means, as in Example 2.2, spin singlet[13] $S = 0$ for the two electrons in any covalent bonding. Note that the perturbation treatment presented here fails when the two atoms are close together. Then, $\alpha E_G, \beta, t$ are no longer small, so the LCAO method should be modified to include higher lying atomic orbitals. As the last remark in this context, this energy lowering mechanism also provides a qualitative picture for "metallic bonding" in metal substances, as described by the "tight binding band theory" for electrons in solids.

Another relevant example is the ammonia molecule, NH_3, schematically shown below.



Chemists would tell you that the ammonia molecule looks like above. From what we have learned so far, it may seem a little strange that the ammonia molecule actually looks like that, as it is highly asymmetric! All stationary states that we have been dealing with are symmetric, and for a good reason, namely the parity symmetry. This ammonia molecule is not symmetric. Why? The answer is that this state is actually not a stationary state.

Let us define the plane formed by the three Hydrogen ions as the xy plane. Since the Hamiltonian to describe this molecule is the sum of kinetic energy terms and Coulomb potential terms, it is a function of $\partial/\partial x_i^2$ and $|\vec{x}_i - \vec{x}_j|$, where $\vec{x}_i, \vec{x}_j$ are coordinates for electrons and nuclei. It is easy to see then that the Hamiltonian is invariant under the parity transformation $(\vec{x}_i)_3 \to -(\vec{x}_i)_3$ for all i. Now apply this parity operation to the above picture, and you get a totally different state in which the Nitrogen ion is below the xy plane. Let us call this state $|2\rangle$ and the original state $|1\rangle$. From the parity symmetry of the Hamiltonian, it is obvious that the energies of these two states are equal. Now, if there is no tunneling amplitude, i.e. no Hamiltonian matrix element, between the two states, then we have nothing to worry about, as states $|1\rangle$ and $|2\rangle$ are, then, stationary states[14]. However, the fact is that our QM common sense tells us[15] that there *should* be a tunneling between states $|1\rangle$ and $|2\rangle$. Indeed there is! Actually, if you start from the above state, then it is known *experimentally* that the molecule oscillates between $|1\rangle$ and $|2\rangle$ with a frequency of 24 GHz, which is in the microwave range. Historically, the first MASER ("microwave laser") was invented making use of this resonance frequency, and subsequent work led to the discovery of LASER, so this oscillation is of historical importance. Now, 24 GHz is a very small energy scale.

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[12] In this picture, we have dealt with attractive potential only. In reality, there is a proton-proton repulsion (for H_2) or a core-core repulsion (for other molecules such as O_2). The repulsive interaction balances the attractive interaction to determine the equilibrium bond length.

[13] It is best to not mix this discussion with "exchange effect," which usually refers to the "exchange interaction." The mechanism here is best described as a formation of a molecular bonding orbital, whose bonding energy arises from the hopping/tunneling matrix element. I advise caution on this point if you read Section 5.1.2 of Griffiths.

[14] They are in this case degenerate stationary states, as are any two linear combinations of $|1\rangle$ and $|2\rangle$. For an unsymmetrical state such as $|1\rangle$ or $|2\rangle$ to be a stationary state, there has to be a degeneracy.

[15] A related common wisdom in QM is that "Nature doesn't like degeneracy."

It corresponds to ~ 0.1 meV in energy, and a mere ~ 1 K in temperature. This is the energy separation between the bonding state $|B\rangle$ and the anti-bonding state $|A\rangle$ described above[16], and so at room temperature the bonding and anti-bonding states are completely mixed together. If you cool down ammonia molecules well below 1 K and isolate them from radiation, they should exist in the bonding state only.

4. Entanglement – Quantum Mechanics at the Edge?

Einstein, Podolsky, and Rosen (EPR) posed the following famous question ("paradox"). Suppose there are two photons, flying opposite to each other. Suppose that their circular polarizations (i.e. spins) are correlated[17] in such a way that the total spin is 0. As in Example 2.3, the total wave function for two photons can be written as, with a sign change due to the boson nature of the photon,

$$|\Psi\rangle = \frac{1}{2}(|k,-k\rangle - |-k,k\rangle)(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

where k is the momentum along the line of motion. Suppose Alice is waiting on one side, and Bob is waiting on the other side, each with a circular polarizer that can measure the polarization of an incoming photon. What is more, suppose Alice is at one end our galaxy and Bob is at the other end. Suppose Alice measures that the spin for her photon is up, and Bob has not measured his photon yet. The question is the following.

$$\boxed{\text{What happens to the wave function } |\Psi\rangle\text{, at the instant that Alice's equipment records } \uparrow\text{?}}$$

The answer indicated by experiments so far is:

$$\boxed{|\Psi\rangle \text{ collapses instantly to } |\Psi_{new}\rangle = |k,-k\rangle|\uparrow\downarrow\rangle.}$$

assuming that Alice's side is on the positive axis of the motion, and assuming, without loss of generality, that Alice measures the first coordinates. What this means is that Bob's equipment will then *certainly* record $|\downarrow\rangle$. The catch here is that Bob does not know what Alice measured, and so it is not the case that any real information is instantly communicated from Alice to Bob. They would know that their results are correlated only if they compare their data later. Despite this, there is a certain mystery in this, to say the least, and one might think that there is something wrong or incomplete about this whole quantum mechanics business. Einstein certainly thought so.

This curious discussion here is possible since $|\Psi\rangle$ is an *entangled state*, a state in which the two particle wave function cannot be separated into a product of two one particle wave functions. That is, $|\Psi\rangle$ cannot be written as $|\psi(1)\rangle|\psi(2)\rangle$, where $1, 2$, as before, mean the coordinates. Consequently, the measurement result on one particle has a *definite correlation* with the measurement result on the other particle, no matter how far apart the two measurements take place.

Einstein expressed his discomfort with this situation by saying that a "spooky action at a distance" does not make sense[18]. The thoughts on this issue made a quantum leap, when Bell published a theorem, in 1964, that says that there is a *measurable difference* between the orthodox quantum mechanics theory (represented by the above answer) and an alternative theory, the local hidden variable theory developed by researchers in the "Einstein school" so to speak. You can read Section 12.2 of Griffiths to learn more about this. Basically, the local hidden variable theory posits that each photon carries all information about future measurements in a function that is dependent on a local hidden variable. Since that function "moves with" the particle, there is no need to invoke any "spooky action at a distance." Before Bell, all hidden variable theories were thought to be

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[16] The energy-time uncertainty principle, again!

[17] I do not claim to know how to prepare such a state. To find out about techniques involved, please look in the literature, e.g. Shih, Rep. Prog. Phys. 66 (2003) 1009–1044.

[18] This discomfort with "spooky action at a distance" is a time-honored tradition of science, which can be summarized by the principle of "causality." Newton also did not like the "spooky" aspect of his gravitation theory and speculated that something more is happening between gravitating objects than just attracting each other at a distance. We are still looking for an experimental verification of that "something," which is supposedly the exchange of gravitons.

consistent with QM, since they were constructed, they thought, as a sort of extension of QM, just having some additional "hidden information." It is considered a remarkable feat that Bell discovered that such a local hidden variable theory and the orthodox quantum mechanics produce different results for certain measurements on EPR pair states. In essence, a local hidden variable theory can be thought of as a theory that believes that there is a "local reality" in Nature even before any measurement. This "reality" was apparently a big concern for Einstein. Experiments so far definitely indicate that the orthodox quantum mechanics is correct since the Bell's results ("Bell's inequality") derived from the local hidden variable theory are not consistent with experiments.

What, then, are the remaining questions? My impression is that we have many philosophical questions, but not really sharp scientific ones that everybody agrees on, although some good scientific questions may be forming in some circles. On one side, we may ask: What is the reality? Since the local hidden variable theory is proven wrong, there must be a non-local hidden variable theory – what then does a "non-local reality" mean? Was there any hole in Bell's theorem? Some controversial papers suggest yes. On the other side, we may ask: If the hidden variable theorists turn out to be right, was the expression "wave function" the greatest misnomer ever? If, on the other hand, the expression "wave function" really is appropriate, what is the nature of the wave? What in the vacuum undulates? Is there any experiment to figure out how the wave function collapse "runs through vacuum," if that is what is happening? Or, is it just a correlation? If so, is the correlation encoded in the wave function in a mathematically nontrivial way that we overlooked so far? Simply put, nobody yet knows the answers to these curious, big, questions.

One of many quotes by Einstein says "For the rest of my life, I will contemplate on what light is." Perhaps, as students of quantum mechanics, but not disrespecting Einstein, we should have our own quote, "*when I can't fall asleep at night, I will contemplate on what the wave function is* (including the wave function for a photon)."

Apart from these issues that seem largely philosophical, or meta-physical, at the moment, quantum mechanics works remarkably well. However, even the best minds, like Einstein's or Feynman's, did not seem to be able to really make peace with the non-intuitive nature of Quantum Mechanics. One may be tempted to think that part of the difficulty is that we are classical creatures with classical concepts and languages and thus we may be limited to *get it* when it comes to ways in which the microscopic world operates. In any case, sharp scientific ways to approach these issues seem not so well defined at present, while good news is that experiments addressing these issues are improving, and the interest in quantum computing and quantum cryptography will also push the field along.

One might say that the rather vague issues described here form the "bleeding edge" of Quantum Mechanics. But, then, what isn't a bleeding edge of science, you might ask. Our world is full of wonders and mysteries for us to discover and solve, and any thing or subject that we think we understand "pretty well" almost always reveal curious, surprising, and novel aspects if we manage to look at it with a careful and serious attitude and the right set of questions. Perhaps the most striking case in point here is the origin of mass. We all start to learn physics using Newton's laws where "mass" appears as a natural quantity. This does not mean that we really know what it is. In fact, one of the leading edge science topics in particle physics at the present time is to address the question "what is mass." Thus, it may not, and it *should not*, sound as bad as it does when we say we do not know what "wave function" or "spin" really means. Also, note that while the word "entanglement" has acquired some mystic flavor to it, the entangled state is actually everywhere, e.g. in all atoms that make us up. In general, any many body wave function, e.g. a Slater determinant (Def. 2.1), ends up being an entangled state. If it is not, that's an exceptional case.

5. One Last Word

State and wave function are different, and so are operator and matrix. Expressions like $\Psi(x) = |lm\rangle$ have been used in this lecture, for pedagogical and notational convenience. Also, expressions like $\hat{H} = \begin{bmatrix} a & b \\ c & b \end{bmatrix}$ have been used in the same spirit. They may have been convenient, but the fact is that they are sloppy/ugly at best and are wrong strictly speaking. Maybe using some other symbol than $=$ may have helped, like using $\mathrel{\overset{\circ}{=}}$ to mean "is represented by" or "represents."

In any case, from now on, please upgrade your notation so that apples and oranges are kept clearly separate. Or at least be very aware of the difference when/if you mix Dirac notation and functions/vectors/matrices. A ket is not a wave function, but a state, namely a physical object (when normalizable). Wave function is a mathematical object that results when the state is projected onto basis states. For instance in the harmonic oscillator problem, we can write $|\Psi\rangle = |n\rangle$ and $\Psi(x) = \langle x|n\rangle = \psi_n(x)$, where $|x\rangle$ is the position eigenstate, but $\Psi(x) = |n\rangle$ is *not* correct since Ψ is a wave function and $|n\rangle$ is a state. Likewise, an operator such as $\hat{O}$ lives in the physical space, i.e. the Hilbert space. A matrix such as $\langle e_i|\hat{O}|e_j\rangle$ is a representation of $\hat{O}$ using a certain basis set, and so it is different from the operator $\hat{O}$ itself.

Put another way, a state or an operator is a unique entity, while its representation, a wave-function/vector or a matrix respectively, is not unique as it changes depending on the basis used. [Please read the last section of the formalism lecture note for more comments.]