Physics 555 Fall 2007
Second quantized notations and conventions

1. A complete **single-particle basis** set $\{\psi_n(\vec{r})\}$ is indicated here in the "r-representation. The notation $\{|n\rangle\}$ denotes the same set of states in a representation-independent way. The notation *n* is meant to indicate a complete set of quantum numbers, including spin, needed to specify the state. The connection formula $\psi_n(\vec{r}) = \langle \vec{r} | n \rangle$ goes from representation-independent form to the r-representation.

2. For a system of Fermions, a complete set of **many-particle basis** functions is indicated by $\{\Psi_{1,2,\ldots}(\vec{r}_a, \vec{r}_b, \cdots)\}$ where any given member of this set is an antisymmetrized product or Slater determinant, of the single particle states $A[\psi_1(\vec{r}_a)\psi_2(\vec{r}_b)\cdots]$, and the subscripts *1, 2,* are short-hand for a set of quantum numbers n_1, n_2 labeling single particle states. Similar to the single-particle case, these states are in r-representation, and a representation-independent version is very convenient, $|n_1, n_2, \cdots\rangle$, where n_1=*0* or *1* indicates the occupancy of the single particle state *1* (short for quantum numbers n_1, *etc*. The notation is terrible – n_1 has two different meanings. I decided intentionally to leave it this way. The reader has to figure out whether occupancies or quantum numbers are under discussion. The connection formula is $\Psi_{1,2,\ldots}(\vec{r}_a, \vec{r}_b, \cdots) = \langle \vec{r}_a, \vec{r}_b, \cdots | n_1, n_2, \cdots \rangle$.

3. The **kinetic energy operator** is $\hat{t} = p^2/2m$ for a single particle, and $\hat{T} = \sum_i p_i^2/2m$ for a collection of identical particles. The coordinate or r-representation, is $-\hbar^2\nabla^2/2m$ for a single particle. The connection formula is a bit tricky. It looks something like $\langle \vec{r}' | \hat{t} | \vec{r} \rangle = -\delta(\vec{r} - \vec{r}')\hbar^2\nabla^2/2m$, but may have to be symmetrized, I didn't check. There is a nice "*n*-representation" formula for this operator in a many-particle system, if a specific single-particle basis $\{|n\rangle\}$ is in use,

$$\hat{T} = \sum_{m,n} \langle m | \hat{t} | n \rangle c_m^+ c_n = \sum_{m,n} \langle m | p^2/2m | n \rangle c_m^+ c_n , \qquad (1)$$

The form obviously changes, depending on the single-particle basis chosen. Here c_n is the lowering operator or destruction operator, that reduces the occupancy of orbital *n* (from *1* to *0* if the initial occupancy was *1*, and multiplies $|\Psi\rangle$ by *0* if the initial occupancy was *0*). The operator c_m^+ is a raising or creation operator. These were defined in HW#7. It is easy to show that for Fermions, the operators obey anticommutation relations $\{c_n, c_m^+\} \equiv c_n c_m^+ + c_m^+ c_n = \delta_{nm}$. To be as simple as possible, suppose the single particle basis is plane waves, which are eigenstates of the kinetic energy. Then the formula is

$$\hat{T} = \sum_k \langle k | p^2/2m | k \rangle c_k^+ c_k = \sum_k (\hbar^2 k^2/2m)\hat{n}_k ,$$

where the number operator is $\hat{n}_k = c_k^+ c_k$. Consider a many particle state which is just a filled Fermi surface of plane-wave states, $|\Psi\rangle = |n_1, n_2, \cdots\rangle$ where *1* means k_1 which is

short for the quantum numbers $\vec{k}_1\sigma_1$. The occupancies n_k are *1* for states with kinetic energy $\hbar^2k^2/2m$ less than $\hbar^2{k_F}^2/2m$, and *0* otherwise. The diagonal matrix elements are $\langle\Psi|\hat{n}_1|\Psi\rangle = \langle n_1, n_2, \cdots|\hat{n}_1|n_1, n_2, \cdots\rangle = n_1$ and $\langle\Psi|\hat{T}|\Psi\rangle = \sum_k \left(\hbar^2k^2/2m\right)n_k$ where n_k is the same Fermi occupancy. These results confirm that eq. (1) is correct in one familiar limit. In fact, this equation is true more generally, for any many-particle operator which is a **sum of single-particle operators**. An example is the density operator $\hat{\rho}_q = \sum_i e^{i\vec{q}\cdot\vec{r}_i}$. This operator is the Fourier transform of $\hat{\rho}(\vec{r}) = \sum_i \delta(\vec{r} - \vec{r}_i)$, and takes the form

$$\hat{\rho}_q = \sum_{m,n} \langle m|e^{i\vec{q}\cdot\vec{r}}|n\rangle c_m^+ c_n \qquad (2)$$

Analogous to the discussion above of kinetic energy, let us use the plane waves as basis functions. The operator $e^{i\vec{q}\cdot\vec{r}}$ has an off-diagonal matrix element connecting any basis function (bra)$|k\rangle$ to the function (ket) $\langle k+q|$, where k is as before, short for $\vec{k}\sigma$. In this basis, therefore, eq. (2) becomes $\hat{\rho}_q = \sum_k \langle k+q|e^{i\vec{q}\cdot\vec{r}}|k\rangle c_{k+q}^+ c_k = \sum_k c_{k+q}^+ c_k$. By the rules of the raising and lowering operators (given in HW#7), one can find the matrix elements $\langle\Psi'|\hat{\rho}_q|\Psi\rangle$ of $\hat{\rho}_q$ in many particle states. If these states are single Slater determinants of plane-wave states, then $\langle\Psi'|\hat{\rho}_q|\Psi\rangle$ is 1 if (a) the single particle state $|k\rangle$ is occupied and $|k+q\rangle$ is unoccupied in $|\Psi\rangle$, and (b) the single particle state $|k+q\rangle$ is occupied and $|k\rangle$ is unoccupied in $|\Psi'\rangle$. Otherwise $\langle\Psi'|\hat{\rho}_q|\Psi\rangle$ is 0. In other words, the operator $c_{k+q}^+ c_k$ changes a state $|\Psi\rangle$ which has the single particle state $|k\rangle$ occupied and $|k+q\rangle$ unoccupied, into a state $|\Psi'\rangle$ with the reverse occupancies.

4. **Operators that act on two particles at a time**. The main example is the Coulomb interaction. This can be written as the sum of products of single-particle operators,

$$H_{\text{int}} = \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} = \frac{1}{2}\int\int d\vec{r}\,d\vec{r}\,'\frac{\hat{\rho}(\vec{r})\hat{\rho}(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} = \frac{1}{2}\sum_q \frac{4\pi e^2}{Vq^2}\hat{\rho}_{-q}\hat{\rho}_q \qquad (3)$$

The operators $\hat{\rho}_q$ and $\hat{\rho}_{-q}$ have the explicit form of eq. (2) in any one-particle basis set. Therefore, in the plane-wave basis we have

$$H_{\text{int}} = \frac{1}{2}\sum_q \frac{4\pi e^2}{Vq^2}\sum_{k'} c_{k'-q}^+ c_{k'}\sum_k c_{k+q}^+ c_k\,,$$

While in a general basis we could write

$$H_{\text{int}} = \frac{1}{2}\sum_q \frac{4\pi e^2}{Vq^2}\sum_{m',n'}\langle m'|e^{-i\vec{q}\cdot\vec{r}}|n'\rangle c_{m'}^+ c_{n'}\sum_{m,n}\langle m|e^{i\vec{q}\cdot\vec{r}}|n\rangle c_m^+ c_n$$

Actually, there is an error in the second and third versions of eq. 3 which propagated into the subsequent equations, namely, the $i \neq j$ restriction was ignored. An incorrect self-interaction was added. When this is fixed, and the anticommutation relations of Fermion operators is used, we find the correct formulas are

$$H_{\text{int}} = \frac{1}{2}\sum_q \frac{4\pi e^2}{Vq^2}\sum_{k,k'} c^+_{k'-q}c^+_{k+q}c_k c_{k'} \tag{4}$$

$$H_{\text{int}} = \frac{1}{2}\sum_q \frac{4\pi e^2}{Vq^2}\sum_{m,n,m',n'} \langle m'|e^{-i\vec{q}\cdot\vec{r}}|n'\rangle\langle m|e^{i\vec{q}\cdot\vec{r}}|n\rangle c^+_{m'}c^+_m c_n c_{n'} \tag{5}$$

These two formulas can be regarded as examples of a general formula

$$H_{\text{int}} = \frac{1}{2}\sum_{m,n,m',n'} \langle m'm|V_{Coulomb}|n'n\rangle c^+_{m'}c^+_m c_n c_{n'}, \tag{6}$$

where in r-space, the matrix element is

$$\langle m'm|V_{Coulomb}|n'n\rangle = \int\int d\vec{r}\,d\vec{r}\,'\psi^*_{m'}(\vec{r}\,')\psi^*_m(\vec{r})\frac{e^2}{|\vec{r}-\vec{r}\,'|}\psi_n(\vec{r})\psi_{n'}(\vec{r}\,'). \tag{7}$$

The formulas (6) and (7) represent the general solution to the question of how to represent a two-particle operator in terms of the many body basis functions written in a particular single-particle basis.

5. Hartree-Fock theory. The aim of HF theory is to find the single particle orbitals $|n\rangle$ for which the Slater determinant $|\Psi\rangle$ (with N orbitals $|n\rangle$ occupied, $|\Psi\rangle = |1,1,\cdots,1,0,0,\cdots\rangle$) has the lowest energy $E = \langle\Psi|H|\Psi\rangle$. For states $|\Psi\rangle$ of this type, the **diagonal** expectation value of the single-particle part of the Hamiltonian (an operator like eq. (1) or (2)),

$$\hat{H}_1 = \sum_i \hat{h}_i = \sum_i \left|p_i^{\,2}/2m + V(\vec{r}_i)\right| = \sum_{mn}\langle m|\hat{h}|n\rangle c^+_m c_n$$

is zero except for terms with m=n. This is because the state $c^+_m c_n|\Psi\rangle$ is orthogonal to $|\Psi\rangle$ unless m=n. Thus we can write for such a Hartree-Fock state,

$$\langle\Psi|\hat{H}_1|\Psi\rangle = \sum_n \langle n|\hat{h}|n\rangle\langle\Psi|c^+_n c_n|\Psi\rangle = \sum_n^{occ}\langle n|p^2/2m + V(\vec{r})|n\rangle \tag{8}$$

Similarly, the diagonal expectation value of the two-particle part of the Hamiltonian involves the quantities $\langle\Psi|c^+_{m'}c^+_m c_n c_{n'}|\Psi\rangle$. But $c^+_{m'}c^+_m c_n c_{n'}|\Psi\rangle$ is almost always orthogonal to $|\Psi\rangle$, unless the same two states n,n' that are destroyed, are recreated. Thus the pair n,n' and the pair m,m' must be the same, which can happen two ways. Either (a) $m' = n'$ and $m = n$, in which case $c^+_n c^+_n c_n c_{n'}|\Psi\rangle = |\Psi\rangle$, or else (b) $m' = n$ and $m = n'$, in which case $c^+_n c^+_{n'} c_n c_{n'}|\Psi\rangle = -|\Psi\rangle$. The opposite signs, reflecting the Pauli principle, come from the anticommutation relations of the operators. Thus we can write

$$\langle\Psi|\hat{H}_{\text{int}}|\Psi\rangle = \sum_{n,n'}^{occ}\left[\langle n'n|V_{Coulomb}|n'n\rangle - \langle nn'|V_{Coulomb}|n'n\rangle\right] \tag{9}$$

Of course, these same two equations (8,9) are normally derived not by using second quantized notations, but from Slater determinants directly. The Hartree-Fock equations follow if we seek the orbitals $|n\rangle$ which minimize the total energy expectation value, the sum of eqs. (8) and (9), under the constraint of ortho-normalization. A slightly different view of Hartree-Fock theory is in the notes on Mean Field Theory.