Física de Semiconductores

Lección 9

Matrix elements

- Let the states $\left|\mu\right\rangle$ be a complete basis for the quantum states of a particle. Then

$$I = \sum_{\mu} \left|\mu\right\rangle\left\langle\mu\right|$$

- Therefore, we can write

$$V = IVI = \sum_{\mu,\mu'} \left|\mu\right\rangle\left\langle\mu\right|V\left|\mu'\right\rangle\left\langle\mu'\right| = \sum_{\mu,\mu'} \left\langle\mu\right|V\left|\mu'\right\rangle\left|\mu\right\rangle\left\langle\mu'\right|$$

- If the system is in state $\left|\mu'\right\rangle$, what $\left|\mu\right\rangle\left\langle\mu'\right|$ does is move the particle from state μ' to state μ.

Creation and annihilation

- We can say that the particle in state μ' is annihilated and a particle in state μ is created.
- To pursue this idea, we define a "vacuum" state $\left|0\right\rangle$ that is orthogonal to all states and normalized so that $\left\langle 0\middle|0\right\rangle = 1$
- Then $\left|\mu\right\rangle\left\langle\mu'\right| = \left|\mu\right\rangle\left\langle 0\middle|0\right\rangle\left\langle\mu'\right| = c_\mu^\dagger c_{\mu'}$
- where we have defined the creation and annihilation operators $c_\mu = \left|0\right\rangle\left\langle\mu\right|; \quad c_\mu^\dagger = \left|\mu\right\rangle\left\langle 0\right|$ so that

$$V = \sum_{\mu,n'} \left\langle\mu\middle|V\middle|\mu'\right\rangle c_\mu^\dagger c_{\mu'}$$

Criticism

- WTF?
- **Answer**: really overkill so far.
- Where does the vacuum state come from? Didn't we say that the $\left\{\left|\mu\right\rangle\right\}$ set was complete?
- **Answer**: Operators actually act on a different Hilbert space: $\left|0\right\rangle \oplus \left\{\left|\mu\right\rangle\right\}$
- This is called a Fock space.

States in Fock space

- We can indicate the states in Fock space as

$$\left|0\right\rangle \equiv \left|0,0.....0,0\right\rangle$$

$$\left|\mu\right\rangle \equiv \left|0,0....1_{\mu},0_{\nu}..0,0\right\rangle$$

$$\left|\nu\right\rangle \equiv \left|0,0....0_{\mu},1_{\nu}..0,0\right\rangle$$

- But how do we interpret states of the form

$$\left|\mu,\nu\right\rangle \equiv \left|0,0....1_{\mu},1_{\nu}..0,0\right\rangle$$

Generalization to 2 particles

- We interpret states of the form

$$\left|\mu,\nu\right\rangle \equiv \left|0,0....1_{\mu},1_{\nu}..0,0\right\rangle$$

- as kets in a extended Fock space of the form

$$\left|0\right\rangle \oplus \left\{\left|\mu\right\rangle\right\} \oplus \left\{\left|\mu\right\rangle\right\} \otimes \left\{\left|\nu\right\rangle\right\}$$

- These will be useful to describe two-particle states…

Generalization to *N* particles

- We interpret states of the form

$$\left|0, l_{\lambda}, 0, \ldots, m_{\mu}, 0, \ldots n_{\nu} .. 0, 0\right\rangle$$

- as representing states for *l+m+n=N* particles in a generalized Fock space of the form

$$\left|0\right\rangle \oplus \left\{\left|\lambda\right\rangle\right\} \oplus \left\{\left|\lambda\right\rangle\right\} \otimes \left\{\left|\mu\right\rangle\right\} \oplus \left\{\left|\lambda\right\rangle\right\} \otimes \left\{\left|\mu\right\rangle\right\} \otimes \left\{\left|\nu\right\rangle\right\} \ldots\ldots$$

- Note that states with different number of particles belong to different "terms" in the direct sum of Hilbert spaces, and therefore are orthogonal by virtue of the definition of inner product in a direct sum.

Two-particle hamiltonian

- Notation $x_i = \left(\boldsymbol{r}_i, s_i\right); \quad \int dx \equiv \sum_s \int d\boldsymbol{r}$

$$\left[-\frac{\hbar^2}{2m}\nabla^2_{\boldsymbol{r}_1} - \frac{\hbar^2}{2m}\nabla^2_{\boldsymbol{r}_2} + V\left(x_1\right) + V\left(x_2\right)\right]\Psi\left(x_1, x_2\right) = E\Psi\left(x_1, x_2\right)$$

- Propose $\Psi\left(x_1, x_2\right) = \varphi_\mu\left(x_1\right)\varphi_\nu\left(x_2\right)$
- Insert:

$$\varphi_\nu\left(x_2\right)\left[-\frac{\hbar^2}{2m}\nabla^2_{\boldsymbol{r}_1}\varphi_\mu\left(x_1\right) + V\left(x_1\right)\varphi_\mu\left(x_1\right)\right] +$$

$$+\varphi_\mu\left(x_1\right)\left[-\frac{\hbar^2}{2m}\nabla^2_{\boldsymbol{r}_2}\varphi_\nu\left(x_2\right) + V\left(x_2\right)\varphi_\nu\left(x_2\right)\right] = E\varphi_\mu\left(x_1\right)\varphi_\nu\left(x_2\right)$$

Two-particle solution

If the ϕ's are eigenfunctions of their respective one-particle hamiltonians

$$\varphi_\nu\left(x_{12}\right)E_\mu\varphi_\mu\left(x_1\right)+\varphi_\mu\left(x_1\right)E_\nu\varphi_\nu\left(x_2\right)=E\varphi_\mu\left(x_1\right)\varphi_\nu\left(x_2\right)$$

which means the the product wavefunction is an eigenstate of the two-particle hamiltonian with energy:

$$E=E_\mu+E_\nu$$

Fermions

- The wave function of a system of *N* electrons must have the symmetry property

$$\Psi\left(x_1,\ldots,x_j,\ldots,x_k,\ldots,x_N\right) = -\Psi\left(x_1,\ldots,x_k,\ldots,x_j,\ldots,x_N\right)$$

- For 2-particles, $\Psi\left(x_1,x_2\right) = \varphi_\mu\left(x_1\right)\varphi_\nu\left(x_2\right)$ lacks this property, but the following is OK:

$$\Psi\left(x_1,x_2\right) = \frac{1}{\sqrt{2}}\left[\varphi_\mu\left(x_1\right)\varphi_\nu\left(x_2\right) - \varphi_\mu\left(x_2\right)\varphi_\nu\left(x_1\right)\right]$$

Slater determinants

- A general antisymmetric function can be written as a Slater determinant

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_\mu(x_1) & \cdots & \varphi_\mu(x_N) \\ \vdots & \vdots & \vdots \\ \varphi_\nu(x_1) & & \varphi_\nu(x_N) \end{vmatrix}$$

- To avoid the wave function being zero, all states μ,ν should be different.
- If there are interaction terms, this function is not an eigenfunction of the entire hamiltonian, but the true wavefunction is a linear combination of all possible *N*-particle Slater determinants.

Orthogonality of Slater determinants (I)

- If $$\Psi = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_\lambda(x_1) & \varphi_\lambda(x_2) \\ \varphi_\mu(x_1) & \varphi_\mu(x_2) \end{vmatrix} =$$

$$= \frac{1}{\sqrt{2}} \left[\varphi_\lambda(x_1)\varphi_\mu(x_2) - \varphi_\lambda(x_2)\varphi_\mu(x_1) \right]$$

- and $$\Phi = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_\lambda(x_1) & \varphi_\lambda(x_2) \\ \varphi_\nu(x_1) & \varphi_\nu(x_2) \end{vmatrix} =$$

$$= \frac{1}{\sqrt{2}} \left[\varphi_\lambda(x_1)\varphi_\nu(x_2) - \varphi_\lambda(x_2)\varphi_\nu(x_1) \right]$$

Orthogonality of Slater determinants (II)

- Then

$$\left\langle \Psi \middle| \Phi \right\rangle = \frac{1}{2}\int dx_1 \int dx_2 \left[\varphi_\lambda^*\left(x_1\right)\varphi_\mu^*\left(x_2\right) - \varphi_\lambda^*\left(x_2\right)\varphi_\mu^*\left(x_1\right)\right]\times$$

$$\left[\varphi_\lambda\left(x_1\right)\varphi_\nu\left(x_2\right) - \varphi_\lambda\left(x_2\right)\varphi_\nu\left(x_1\right)\right]$$

$$= \frac{1}{2}\Big[\int dx_1\, dx_2 \varphi_\lambda^*\left(x_1\right)\varphi_\mu^*\left(x_2\right)\varphi_\lambda\left(x_1\right)\varphi_\nu\left(x_2\right) -$$

$$\int dx_1\, dx_2 \varphi_\lambda^*\left(x_1\right)\varphi_\mu^*\left(x_2\right)\varphi_\lambda\left(x_2\right)\varphi_\nu\left(x_1\right) -$$

$$\int dx_1\, dx_2 \varphi_\lambda^*\left(x_2\right)\varphi_\mu^*\left(x_1\right)\varphi_\lambda\left(x_1\right)\varphi_\nu\left(x_2\right) +$$

$$\int dx_1\, dx_2 \varphi_\lambda^*\left(x_2\right)\varphi_\mu^*\left(x_1\right)\varphi_\lambda\left(x_2\right)\varphi_\nu\left(x_1\right)\Big] = 0$$

Orthogonality of Slater determinants (III)

- Two Slater determinants are orthogonal unless they contain the **same set** of one-electron wave functions.

Occupation number representation for fermions

- Because of the antisymmetry requirement, we only need to consider states of the form.

$$\left|0,0....1_{\mu},1_{\nu}..0,0\right\rangle$$

- which correspond to a wave function given by a Slater determinant of the form

$$\Psi = \frac{1}{\sqrt{2!}}\begin{vmatrix} \varphi_{\mu}\left(x_1\right) & \varphi_{\mu}\left(x_2\right) \\ \varphi_{\nu}\left(x_1\right) & \varphi_{\nu}\left(x_2\right) \end{vmatrix}$$

Possible ambiguity

- There is an ambiguity because

$$\left|0,0....1_{\mu},1_{\nu}..0,0\right\rangle$$

- could mean

$$\Psi_{\text{option 1}} = \frac{1}{\sqrt{2!}}\begin{vmatrix} \varphi_{\mu}\left(x_1\right) & \varphi_{\mu}\left(x_2\right) \\ \varphi_{\nu}\left(x_1\right) & \varphi_{\nu}\left(x_2\right) \end{vmatrix}$$

- or

$$\Psi_{\text{option 2}} = \frac{1}{\sqrt{2!}}\begin{vmatrix} \varphi_{\nu}\left(x_1\right) & \varphi_{\nu}\left(x_2\right) \\ \varphi_{\mu}\left(x_1\right) & \varphi_{\mu}\left(x_2\right) \end{vmatrix} = -\Psi_{\text{option 1}}$$

- This is just a phase factor exp(iπ), which is irrelevant as long as we apply it consistently.

Eliminate ambiguity

- To avoid errors associated with changing phase convention in the middle of a calculation, we eliminate the ambiguity by ordering the states using an index ν_j so that

$$\left|0_1,1_2,0_3,1_4,0_5,1_6,0_7\right\rangle \Rightarrow \frac{1}{\sqrt{3}}\begin{vmatrix} \varphi_{\nu_2}(x_1) & \varphi_{\nu_2}(x_2) & \varphi_{\nu_2}(x_3) \\ \varphi_{\nu_4}(x_1) & \varphi_{\nu_4}(x_2) & \varphi_{\nu_4}(x_3) \\ \varphi_{\nu_6}(x_1) & \varphi_{\nu_6}(x_2) & \varphi_{\nu_6}(x_3) \end{vmatrix}$$

- Therefore, there is **one and only one** Slater determinant associated with an occupation number ket, and it is given by the above convention.

Generic occupation states

- We introduce the notation

$$\left|\left\{n_\mu\right\}\right\rangle \equiv \left|n_1, n_2, n_3, \ldots.\right\rangle$$

- to represent the many-electron kets.
- Remember: all *n*'s are either 0 or 1, states are orthogonal if the sum of *n*'s is different, and states are orthogonal if the *n* =1 appear for different states μ

$$\left\langle\left\{n_\mu\right\}\middle|\left\{n_{\mu'}\right\}\right\rangle = 0; \quad \left\langle\left\{n_\mu\right\}\middle|\left\{n_\mu\right\}\right\rangle = 1$$

Operators in Fock space

- Since the $\left|\left\{n_\mu\right\}\right\rangle$ form a complete set in Fock space:

$$I = \sum_{\left\{n_\mu\right\}} \left|\left\{n_\mu\right\}\right\rangle\left\langle\left\{n_\mu\right\}\right|$$

$$V = \sum_{\left\{n_\mu\right\},\left\{n_{\mu'}\right\}} \left|\left\{n_\mu\right\}\right\rangle\left\langle\left\{n_\mu\right\}\right| V \left|\left\{n_{\mu'}\right\}\right\rangle\left\langle\left\{n_\mu{}'\right\}\right|$$

$$= \sum_{\left\{n_\mu\right\},\left\{n_{\mu'}\right\}} V_{\mu\mu'} \left|\left\{n_\mu\right\}\right\rangle\left\langle\left\{n_\mu{}'\right\}\right|; \quad V_{\mu\mu'} \equiv \left\langle\left\{n_\mu\right\}\right| V \left|\left\{n_{\mu'}\right\}\right\rangle$$

Creation/annihilation operators

- Similarly to what we did in the one-particle Fock space, we can define creation and annihilation operators in the many-particle Fock space using the $\left|\left\{n_\mu\right\}\right\rangle$ states.
- The simplest such operators would change the occupation number of just one state, for example

$$\left|n_1, n_2, \ldots, n_p = 1, \ldots\right\rangle\left\langle n_1, n_2, \ldots, n_p = 0, \ldots\right|$$

$$\left|n_1, n_2, \ldots, n_p = 0, \ldots\right\rangle\left\langle n_1, n_2, \ldots, n_p = 1, \ldots\right|$$

Creation operators (I)

- If we want the operator to act on any state by increasing the occupation of the state *p*, we would have to write

$$c_p^\dagger = \sum_{\{n_i\}(i\neq p)} \left|\ldots, n_p = 1, \ldots\right\rangle\left\langle\ldots, n_p = 0, \ldots\right|$$

- However, it is customary to use a different convention. This convention greatly facilitates the calculation of matrix elements, as we will see later. It is based on assuming that the creation operator adds the new state **to the top row of the corresponding Slater determinant**.

Creation operators (II)

- Therefore, the state $c_3^\dagger c_2^\dagger c_1^\dagger \left|0\right\rangle$ corresponds to the Slater determinant

$$\begin{vmatrix} \varphi_3(1) & \varphi_3(2) & \varphi_3(3) \\ \varphi_2(1) & \varphi_2(2) & \varphi_2(3) \\ \varphi_1(1) & \varphi_1(2) & \varphi_1(3) \end{vmatrix}$$

- But the state $\left|1_1, 1_2, 1_3\right\rangle$ corresponds to

$$\begin{vmatrix} \varphi_1(1) & \varphi_1(2) & \varphi_1(3) \\ \varphi_2(1) & \varphi_2(2) & \varphi_2(3) \\ \varphi_3(1) & \varphi_3(2) & \varphi_3(3) \end{vmatrix}$$

Therefore

$$c_3^\dagger c_2^\dagger c_1^\dagger \left|0\right\rangle = -\left|1_1, 1_2, 1_3\right\rangle$$

Example

$$\left|1_1,0_2,0_3,1_4\right\rangle \Rightarrow \begin{vmatrix} \varphi_1(x_1) & \varphi_1(x_2) \\ \varphi_4(x_1) & \varphi_4(x_2) \end{vmatrix}$$

$$c_3^\dagger \left|1_1,0_2,0_3,1_4\right\rangle \Rightarrow \begin{vmatrix} \varphi_3(x_1) & \varphi_3(x_2) & \varphi_3(x_3) \\ \varphi_1(x_1) & \varphi_1(x_2) & \varphi_1(x_3) \\ \varphi_4(x_1) & \varphi_4(x_2) & \varphi_4(x_2) \end{vmatrix}$$

$$= (-1)\begin{vmatrix} \varphi_1(x_1) & \varphi_1(x_2) & \varphi_1(x_3) \\ \varphi_3(x_1) & \varphi_3(x_2) & \varphi_3(x_3) \\ \varphi_4(x_1) & \varphi_4(x_2) & \varphi_4(x_2) \end{vmatrix} = -\left|1_1,0_2,1_3,1_4\right\rangle$$

Phase convention

- The phase convention can be written as follows. Define $N_p = \sum_{j=1}^{p-1} n_j$ and

$$c_p^\dagger = \sum_{\{n_i\}(i \neq p)} (-1)^{N_p} \left| \ldots, n_p = 1, \ldots \right\rangle \left\langle \ldots, n_p = 0, \ldots \right|$$

- In our example, $N_3 = n_1 + n_2 = 1 + 0 = 1$

Annihilation operator

- The adjoint of the creation operator is

$$c_p = \sum_{\{n_i\}(i \neq p)} \left(-1\right)^{N_p} \left| \ldots, n_p = 0, \ldots \right\rangle \left\langle \ldots, n_p = 1, \ldots \right|$$

- Then it is apparent that such operators remove states, so they are called annihilation operators.
- The definition implies that the annihilation operator removes a state from the top row of the Slater determinant, so the state has to be moved to that position to be ready to be destroyed.

Example

$$\begin{vmatrix} \varphi_4(x_1) & \varphi_4(x_2) & \varphi_4(x_3) \\ \varphi_1(x_1) & \varphi_1(x_2) & \varphi_1(x_3) \\ \varphi_3(x_1) & \varphi_3(x_2) & \varphi_3(x_2) \end{vmatrix} = (-1) \begin{vmatrix} \varphi_1(x_1) & \varphi_1(x_2) & \varphi_1(x_3) \\ \varphi_4(x_1) & \varphi_4(x_2) & \varphi_4(x_3) \\ \varphi_3(x_1) & \varphi_3(x_2) & \varphi_3(x_2) \end{vmatrix}$$

$$= (-1)(-1) \begin{vmatrix} \varphi_1(x_1) & \varphi_1(x_2) & \varphi_1(x_3) \\ \varphi_3(x_1) & \varphi_3(x_2) & \varphi_3(x_3) \\ \varphi_4(x_1) & \varphi_4(x_2) & \varphi_4(x_2) \end{vmatrix} \Rightarrow (-1)(-1) \left| 1_1, 0_2, 1_3, 1_4 \right\rangle$$

Therefore we define

$$c_4 \left| 1_1, 0_2, 1_3, 1_4 \right\rangle = (-1)(-1) \left| 1_1, 0_2, 1_3, 0_4 \right\rangle = \left| 1_1, 0_2, 1_3, 0_4 \right\rangle$$

Properties of operators I

- If we apply the creation operator *p* to a state with *p*=1, we have terms of the form

$$\left|...,n_p=1,...\right\rangle\left\langle...,n_p=0,...\right\|...,n_p=1,...\rangle=0$$

- Therefore

$$c_p^\dagger\left|...,n_p=1,...\right\rangle=0$$

- Similarly

$$c_p\left|...,n_p=0,...\right\rangle=0$$

Properties of operators II

- If we apply the creation operator twice, we have terms of the form

$$\left|...,n_p=1,...\right\rangle\left\langle...,n_p=0,...\right|\left|...,n_p=1,...\right\rangle\left\langle...,n_p=0,...\right|=0$$

- Therefore

$$c_p^\dagger c_p^\dagger = 0$$

- Similarly

$$c_p c_p = 0$$

Number operator I

- We now consider the operator

$$c_p^\dagger c_p =$$

$$\sum_{\{n_i\}(i\neq p)} \left(-1\right)^{N_p} \left|\ldots, n_p = 1, \ldots\right\rangle \left\langle \ldots, n_p = 0, \ldots\right| \sum_{\{n_i\}(i\neq p)} \left(-1\right)^{N_p} \left|\ldots, n_p = 0, \ldots\right\rangle \left\langle \ldots, n_p = 1, \ldots\right|$$

- If we apply it to a state $\left|\alpha\right\rangle \equiv \left|n_1, n_2, \ldots, n_p = 1, \ldots\right\rangle$

$$c_p^\dagger c_p =$$

$$\sum_{\{n_i\}(i\neq p)} \left(-1\right)^{N_p} \left|\ldots, n_p = 1, \ldots\right\rangle \left\langle \ldots, n_p = 0, \ldots\right| \left(-1\right)^{N_p} \left|n_1, n_2, \ldots, n_p = 0, \ldots\right\rangle$$

$$= \left(-1\right)^{N_p\left(\left|\alpha\right\rangle\right)} \left(-1\right)^{N_p\left(\left|\alpha\right\rangle\right)} \left|n_1, n_2, \ldots, n_p = 1, \ldots\right\rangle = \left|n_1, n_2, \ldots, n_p = 1, \ldots\right\rangle$$

Number operator II

If we apply it to a state $\left| n_1, n_2, \ldots, n_p = 0, \ldots \right\rangle$

$$c_p^\dagger c_p = 0$$

Because c_p acting on a p-empty state gives zero.

Therefore the operator $c_p^\dagger c_p$ gives 1 if the state is occupied and zero if the state is empty, and therefore it is called the number operator.

Reverse number operator

- Similarly, we can also show that the operator $c_p c_p^\dagger$ gives 1 if the state *p* is empty and 0 if the state is filled, so that

$$c_p c_p^\dagger = 1 - n_p = 1 - c_p^\dagger c_p$$

- or

$$\left\{ c_p^\dagger, c_p \right\} \equiv c_p^\dagger c_p + c_p c_p^\dagger = 1$$

- where { } is the anticonmutator.

Creation/annihilation for $p \neq q$

- Consider now $\left|\alpha\right\rangle = \left|n_1, n_2, .., n_p = 0, ..., n_q = 1...\right\rangle$

$$c_p^\dagger c_q \left|n_1, n_2, .., n_p = 0, ..., n_q = 1...\right\rangle =$$

$$= \sum_{\{n_i\}(i \neq p)} \left(-1\right)^{N_p} \left|..., n_p = 1, ...\right\rangle \left\langle ..., n_p = 0, ...\right| \times$$

$$\sum_{\{n_i\}(i \neq q)} \left(-1\right)^{N_q} \left|..., n_q = 0, ...\right\rangle \left\langle ..., n_q = 1, ...\right| \left|n_1, n_2, .., n_p = 0, ..., n_q = 1...\right\rangle$$

$$= \sum_{\{n_i\}(i \neq p)} \left(-1\right)^{N_p} \left|..., n_p = 1, ...\right\rangle \left\langle ..., n_p = 0, ...\right| \left(-1\right)^{N_q(\left|\alpha\right\rangle)} \left|n_1, n_2, ..., n_p = 0, ...n_q = 0...\right\rangle$$

$$= \left(-1\right)^{N_p} \left(-1\right)^{N_q(\left|\alpha\right\rangle)} \left|n_1, n_2, ..., n_p = 1, ...n_q = 0...\right\rangle$$

- But we have

$$N_p\left(\left|n_1, n_2, ..., n_p = 1, ...n_q = 0...\right\rangle\right) = N_p\left(\left|\alpha\right\rangle\right) \text{ for } p < q$$

$$N_p\left(\left|n_1, n_2, ..., n_p = 1, ...n_q = 0...\right\rangle\right) = N_p\left(\left|\alpha\right\rangle\right) - 1 \text{ for } p > q$$

One creation/one annihilation (II)

- But since for $p \neq q$ either $p<q$ or $p > q$, then the above implies

$$c_p^\dagger c_q = -c_q c_p^\dagger$$

$$c_p^\dagger c_q + c_q c_p^\dagger = 0$$

$$\left\{ c_p^\dagger, c_q \right\} = 0$$

- Or, for general p,q

$$\left\{ c_p^\dagger, c_q \right\} = \delta_{pq}$$

Summary of conmutation relations

$$\left\{c_p^\dagger, c_q^\dagger\right\} = 0$$

$$\left\{c_p, c_q\right\} = 0$$

$$\left\{c_p^+, c_q\right\} = \delta_{pq}$$

One-electron operators I

- We now consider any operator that can be written in coordinate representation

$$\hat{H} = \sum_{i=1}^{N} H\left(\boldsymbol{r}_i\right)$$

- and express this in the occupation number formalism. As indicated before, any operator must be

- $$H = \sum_{\{n_\mu\},\{n_{\mu'}\}} H_{\mu\mu'} \left|\{n_\mu\}\right\rangle \left\langle\{n_\mu{}'\}\right|; \quad H_{\mu\mu'} \equiv \left\langle\{n_\mu\}\right| H \left|\{n_{\mu'}\}\right\rangle$$

Matrix element $H_{\mu\mu'} \equiv \left\langle \left\{ n_\mu \right\} \middle| H \middle| \left\{ n_{\mu'} \right\} \right\rangle$

- This is a matrix element between Slater determinants. To get a sense of what we should expect before we derive a general expression, we will consider the simplest case of 2x2 determinants and calculate the matrix elements explicitly.

2x2 example

- Let us assume

$$\Psi = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_\alpha(\boldsymbol{r}_1) & \varphi_\alpha(\boldsymbol{r}_2) \\ \varphi_\beta(\boldsymbol{r}_1) & \varphi_\beta(\boldsymbol{r}_2) \end{vmatrix}$$

$$\Phi = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_\lambda(\boldsymbol{r}_1) & \varphi_\lambda(\boldsymbol{r}_2) \\ \varphi_\mu(\boldsymbol{r}_1) & \varphi_\mu(\boldsymbol{r}_2) \end{vmatrix}$$

Matrix elements (I)

- Then $\left\langle \Psi \middle| V\left(\boldsymbol{r}_1\right) \middle| \Phi \right\rangle$

$$= \frac{1}{2}\left\{ \int d\boldsymbol{r}_1\, d\boldsymbol{r}_2 \left[\varphi_\alpha^*\left(\boldsymbol{r}_1\right)\varphi_\beta^*\left(\boldsymbol{r}_2\right) - \varphi_\alpha^*\left(\boldsymbol{r}_2\right)\varphi_\beta^*\left(\boldsymbol{r}_1\right) \right] V\left(\boldsymbol{r}_1\right) \times \right.$$

$$\left. \left[\varphi_\lambda\left(\boldsymbol{r}_1\right)\varphi_\mu\left(\boldsymbol{r}_2\right) - \varphi_\lambda\left(\boldsymbol{r}_2\right)\varphi_\mu\left(\boldsymbol{r}_1\right) \right] \right\}$$

$$= \frac{1}{2}\left\{ \int d\boldsymbol{r}_1 \varphi_\alpha^*\left(\boldsymbol{r}_1\right) V\left(\boldsymbol{r}_1\right) \varphi_\lambda\left(\boldsymbol{r}_1\right) \int d\boldsymbol{r}_2 \varphi_\beta^*\left(\boldsymbol{r}_2\right) \varphi_\mu\left(\boldsymbol{r}_2\right) + \right.$$

$$- \int d\boldsymbol{r}_1 \varphi_\alpha^*\left(\boldsymbol{r}_1\right) V\left(\boldsymbol{r}_1\right) \varphi_\mu\left(\boldsymbol{r}_1\right) \int d\boldsymbol{r}_2 \varphi_\beta^*\left(\boldsymbol{r}_2\right) \varphi_\lambda\left(\boldsymbol{r}_2\right) +$$

$$- \int d\boldsymbol{r}_1 \varphi_\beta^*\left(\boldsymbol{r}_1\right) V\left(\boldsymbol{r}_1\right) \varphi_\lambda\left(\boldsymbol{r}_1\right) \int d\boldsymbol{r}_2 \varphi_\alpha^*\left(\boldsymbol{r}_2\right) \varphi_\mu\left(\boldsymbol{r}_2\right) +$$

$$\left. + \int d\boldsymbol{r}_1 \varphi_\beta^*\left(\boldsymbol{r}_1\right) V\left(\boldsymbol{r}_1\right) \varphi_\mu\left(\boldsymbol{r}_1\right) \int d\boldsymbol{r}_2 \varphi_\alpha^*\left(\boldsymbol{r}_2\right) \varphi_\lambda\left(\boldsymbol{r}_2\right) \right\}$$

Matrix elements (I)

- And $\left\langle \Psi \middle| V\left(\boldsymbol{r}_2\right) \middle| \Phi \right\rangle$

$$= \frac{1}{2}\left\{ \int d\boldsymbol{r}_1\, d\boldsymbol{r}_2 \left[\varphi_\alpha^*\left(\boldsymbol{r}_1\right)\varphi_\beta^*\left(\boldsymbol{r}_2\right) - \varphi_\alpha^*\left(\boldsymbol{r}_2\right)\varphi_\beta^*\left(\boldsymbol{r}_1\right) \right] V\left(\boldsymbol{r}_2\right) \times \right.$$

$$\left. \left[\varphi_\lambda\left(\boldsymbol{r}_1\right)\varphi_\mu\left(\boldsymbol{r}_2\right) - \varphi_\lambda\left(\boldsymbol{r}_2\right)\varphi_\mu\left(\boldsymbol{r}_1\right) \right] \right\}$$

$$= \frac{1}{2}\left\{ \int d\boldsymbol{r}_2 \varphi_\beta^*\left(\boldsymbol{r}_2\right) V\left(\boldsymbol{r}_2\right) \varphi_\mu\left(\boldsymbol{r}_2\right) \int d\boldsymbol{r}_1 \varphi_\alpha^*\left(\boldsymbol{r}_1\right)\varphi_\lambda\left(\boldsymbol{r}_2\right) + \right.$$

$$- \int d\boldsymbol{r}_2 \varphi_\beta^*\left(\boldsymbol{r}_2\right) V\left(\boldsymbol{r}_2\right) \varphi_\lambda\left(\boldsymbol{r}_2\right) \int d\boldsymbol{r}_1 \varphi_\alpha^*\left(\boldsymbol{r}_1\right)\varphi_\mu\left(\boldsymbol{r}_1\right) +$$

$$- \int d\boldsymbol{r}_2 \varphi_\alpha^*\left(\boldsymbol{r}_2\right) V\left(\boldsymbol{r}_2\right) \varphi_\mu\left(\boldsymbol{r}_2\right) \int d\boldsymbol{r}_1 \varphi_\beta^*\left(\boldsymbol{r}_1\right)\varphi_\lambda\left(\boldsymbol{r}_1\right) +$$

$$\left. + \int d\boldsymbol{r}_2 \varphi_\alpha^*\left(\boldsymbol{r}_2\right) V\left(\boldsymbol{r}_2\right) \varphi_\lambda\left(\boldsymbol{r}_2\right) \int d\boldsymbol{r}_1 \varphi_\beta^*\left(\boldsymbol{r}_1\right)\varphi_\mu\left(\boldsymbol{r}_1\right) \right\}$$

Lesson 1 from matrix elements

- Due to the orthogonality of the one-electron wave functions, the above matrix elements are zero unless the two Slater determinants share one state.
- For the NxN case, this can be generalized by stating that the Slater determinants in matrix elements of one-electron operators can differ by at most one single-particle state.

Sign of matrix elements

Case α=λ

$$\left\langle \Psi \middle| V\left(\boldsymbol{r}_1\right)+V\left(\boldsymbol{r}_2\right) \middle| \Phi \right\rangle = \tfrac{1}{2}\int d\boldsymbol{r}_1 \varphi_\beta^*\left(\boldsymbol{r}_1\right) V\left(\boldsymbol{r}_1\right) \varphi_\mu\left(\boldsymbol{r}_1\right) +$$

$$\tfrac{1}{2}\int d\boldsymbol{r}_1 \varphi_\beta^*\left(\boldsymbol{r}_2\right) V\left(\boldsymbol{r}_2\right) \varphi_\mu\left(\boldsymbol{r}_2\right) = \int d\boldsymbol{r} \varphi_\beta^*\left(\boldsymbol{r}\right) V\left(\boldsymbol{r}\right) \varphi_\mu\left(\boldsymbol{r}\right)$$

Case α=μ

$$\left\langle \Psi \middle| V\left(\boldsymbol{r}_1\right)+V\left(\boldsymbol{r}_2\right) \middle| \Phi \right\rangle = -\int d\boldsymbol{r}_1 \varphi_\beta^*\left(\boldsymbol{r}_1\right) V\left(\boldsymbol{r}_1\right) \varphi_\lambda\left(\boldsymbol{r}_1\right)$$

Case β=λ

$$\left\langle \Psi \middle| V\left(\boldsymbol{r}_1\right)+V\left(\boldsymbol{r}_2\right) \middle| \Phi \right\rangle = -\int d\boldsymbol{r}_1 \varphi_\alpha^*\left(\boldsymbol{r}_1\right) V\left(\boldsymbol{r}_1\right) \varphi_\mu\left(\boldsymbol{r}_1\right)$$

Case β=μ

$$\left\langle \Psi \middle| V\left(\boldsymbol{r}_1\right)+V\left(\boldsymbol{r}_2\right) \middle| \Phi \right\rangle = \int d\boldsymbol{r}_1 \varphi_\alpha^*\left(\boldsymbol{r}_1\right) V\left(\boldsymbol{r}_1\right) \varphi_\mu\left(\boldsymbol{r}_1\right)$$

General case, Slater-Condon rules

- The Slater-Condon rules state that if I have two Slater determinants Ψ and Φ which differ in one single state which is $\varphi_\gamma\left(x\right)$ for Ψ and $\varphi_\nu\left(x\right)$ for Φ, then for a single electron operator

$$\left\langle \Psi \middle| \hat{H} \middle| \Phi \right\rangle = \left\langle \gamma \middle| H \middle| \nu \right\rangle$$

- provided that the Slater determinants are arranged for "maximum coincidence", so that all identical states occupy the same row in both determinants. This is exactly what happens in the cases α=λ and β=μ in our 2x2 example. But if the states are not in maximum coincidence, the matrix element can change sign, as in the cases α=μ and β=λ.

The matrix element $H_{\mu\mu'} \equiv \left\langle \left\{ n_\mu \right\} \middle| H \middle| \left\{ n_{\mu'} \right\} \right\rangle$

- We are now ready to calculate the matrix element $H_{\mu\mu'}$, For one-electron operators, all matrix elements are zero except those of the form

$$\left\langle ....n_p = 1,...,n_q = 0,... \middle| \hat{H} \middle| ....n_p = 0,...,n_q = 1,... \right\rangle$$

- However, the corresponding Slater determinants are not necessarily arranged for maximum coincidence. For example, I could have 2,5,7 and 2,7,8. The latter would have to be switched to 2,8,7 for maximum coincidence, introducing a factor of -1.

General expression (I)

- To derive a general expression, we note that for the above determinants we need to move the row at position *q* to position *p*. The number of permutations that we need is equal to the number of occupied states between *p* and *q*:

$$N_{pq} = \sum_{j=p+1}^{q-1} n_j = \sum_{j=p}^{q-1} n_j$$

- where the second equality results from n_p=0 for the right-hand state. Notice that using the earlier definition of N_p:

$$N_p + N_{pq} = N_q$$

General expression (II)

- Using the above, we can then write

$$\left\langle ....n_p = 1,...,n_q = 0,... \right| \hat{H} \left| ....n_p = 0,...,n_q = 1,... \right\rangle$$
$$= (-1)^{N_{pq}} \left\langle \varphi_p \right| H \left| \varphi_q \right\rangle$$

- so that

$$\hat{H} = \sum_{\substack{p,q \\ \{n_j\},j\neq p,q}} (-1)^{N_{pq}} \left\langle \varphi_p \right| H \left| \varphi_q \right\rangle \left| ...n_p = 1,...,n_q = 0,... \right\rangle \left\langle ...n_p = 1,...,n_q = 0,.. \right|$$

- but

$$c_p^\dagger c_q = \sum_{\{n_i\}(i\neq p)} \left(-1\right)^{N_p} \left| ...,n_p = 1,... \right\rangle \left\langle ...,n_p = 0,... \right|$$
$$\times \sum_{\{n_i'\}(i\neq q)} \left(-1\right)^{N_q} \left| ...,n_q = 0,... \right\rangle \left\langle ...,n_q = 1,... \right|$$
$$= \sum_{\{n_i\}(i\neq p,q)} \left(-1\right)^{N_p+N_q} \left| ...,n_p = 1,... \right\rangle \left\langle ...,n_q = 1,... \right|$$

General expression (III)

- Finally $\left\langle ....n_p = 1,...,n_q = 0,... \right| \hat{H} \left| ....n_p = 0,...,n_q = 1,... \right\rangle$

$$= \sum_{p,q} (-1)^{N_{pq}} (-1)^{N_p + N_q} \left\langle \varphi_p \right| H \left| \varphi_q \right\rangle c_p^\dagger c_q$$

$$= \sum_{p,q} (-1)^{N_p + N_{pq} + N_q} \left\langle \varphi_p \right| H \left| \varphi_q \right\rangle c_p^\dagger c_q$$

$$= \sum_{p,q} (-1)^{2N_q} \left\langle \varphi_p \right| H \left| \varphi_q \right\rangle c_p^\dagger c_q$$

$$= \sum_{p,q} \left\langle \varphi_p \right| H \left| \varphi_q \right\rangle c_p^\dagger c_q$$

- This shows the utility of the phase factors we introduced in the definition of the *c*'s. They exactly compensate the phase factors from the Slater determinants, making it very easy to compute matrix elements between any two Slater determinants.

Double check (I)

- Now let's double check. We have

$$\Psi = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_\alpha(\boldsymbol{r}_1) & \varphi_\alpha(\boldsymbol{r}_2) \\ \varphi_\beta(\boldsymbol{r}_1) & \varphi_\beta(\boldsymbol{r}_2) \end{vmatrix} = c_\alpha^\dagger c_\beta^\dagger \left|0\right\rangle$$

$$\Phi = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_\lambda(\boldsymbol{r}_1) & \varphi_\lambda(\boldsymbol{r}_2) \\ \varphi_\mu(\boldsymbol{r}_1) & \varphi_\mu(\boldsymbol{r}_2) \end{vmatrix} = c_\lambda^\dagger c_\mu^\dagger \left|0\right\rangle$$

- Therefore $\left\langle \Psi \middle| \hat{H} \middle| \Phi \right\rangle = \left\langle 0 \middle| c_\beta c_\alpha \hat{H} c_\lambda^\dagger c_\mu^\dagger \middle| 0 \right\rangle$

$$\left\langle \Psi \middle| \hat{H} \middle| \Phi \right\rangle = \left\langle 0 \middle| c_\beta c_\alpha \sum_{a,b} \left\langle \varphi_a \middle| H \middle| \varphi_b \right\rangle c_a^\dagger c_b c_\lambda^\dagger c_\mu^\dagger \middle| 0 \right\rangle$$

- This is zero if $\alpha \neq \lambda, \alpha \neq \mu, \beta \neq \lambda, \beta \neq \mu$. Otherwise

Case α=λ

$$\left\langle \Psi \middle| \hat{H} \middle| \Phi \right\rangle = \left\langle 0 \middle| c_\beta \sum_{a,b} \left\langle \varphi_a \middle| H \middle| \varphi_b \right\rangle c_a^\dagger c_b c_\alpha c_\alpha^\dagger c_\mu^\dagger \middle| 0 \right\rangle$$

$$= \left\langle 0 \middle| c_\beta \sum_{a,b} \left\langle \varphi_a \middle| H \middle| \varphi_b \right\rangle c_a^\dagger c_b \left(1 - c_\alpha^\dagger c_\alpha\right) c_\mu^\dagger \middle| 0 \right\rangle$$

$$= \left\langle 0 \middle| c_\beta \sum_{a,b} \left\langle \varphi_a \middle| H \middle| \varphi_b \right\rangle c_a^\dagger c_b c_\mu^\dagger \middle| 0 \right\rangle$$

- If β= μ

$$\left\langle \Psi \middle| \hat{H} \middle| \Phi \right\rangle = \left\langle 0 \middle| \sum_{a,b} \left\langle \varphi_a \middle| H \middle| \varphi_b \right\rangle c_a^\dagger c_b c_\mu c_\mu^\dagger \middle| 0 \right\rangle = \left\langle 0 \middle| \sum_{a,b} \left\langle \varphi_a \middle| H \middle| \varphi_b \right\rangle c_a^\dagger c_b \middle| 0 \right\rangle$$

$$= \sum_a \left\langle \varphi_a \middle| H \middle| \varphi_a \right\rangle$$

- If β≠ μ

$$\left\langle \Psi \middle| \hat{H} \middle| \Phi \right\rangle = \left\langle 0 \middle| c_\beta \sum_{a,b} \left\langle \varphi_a \middle| H \middle| \varphi_b \right\rangle c_a^\dagger c_b c_\mu^\dagger \middle| 0 \right\rangle = \left\langle 0 \middle| c_\beta \sum_a \left\langle \varphi_a \middle| H \middle| \varphi_\mu \right\rangle c_a^\dagger \middle| 0 \right\rangle$$

$$= \left\langle \varphi_\beta \middle| H \middle| \varphi_\mu \right\rangle$$

Case α=μ

$$\left\langle \Psi \middle| \hat{H} \middle| \Phi \right\rangle = -\left\langle 0 \middle| c_\beta \sum_{a,b} \left\langle \varphi_a \middle| H \middle| \varphi_b \right\rangle c_a^\dagger c_b c_\lambda^\dagger c_\mu c_\mu^\dagger \middle| 0 \right\rangle$$

$$= -\left\langle 0 \middle| c_\beta \sum_{a,b} \left\langle \varphi_a \middle| H \middle| \varphi_b \right\rangle c_a^\dagger c_b c_\lambda^\dagger \left(1 - c_\mu^\dagger c_\mu\right) \middle| 0 \right\rangle$$

$$= -\left\langle 0 \middle| c_\beta \sum_{a,b} \left\langle \varphi_a \middle| H \middle| \varphi_b \right\rangle c_a^\dagger c_b c_\lambda^\dagger \middle| 0 \right\rangle$$

- If β= λ

$$\left\langle \Psi \middle| \hat{H} \middle| \Phi \right\rangle = -\left\langle 0 \middle| \sum_{a,b} \left\langle \varphi_a \middle| H \middle| \varphi_b \right\rangle c_a^\dagger c_b c_\lambda c_\lambda^\dagger \middle| 0 \right\rangle = \left\langle 0 \middle| \sum_{a,b} \left\langle \varphi_a \middle| H \middle| \varphi_b \right\rangle c_a^\dagger c_b \middle| 0 \right\rangle$$

$$= -\sum_a \left\langle \varphi_a \middle| H \middle| \varphi_a \right\rangle$$

- If β≠ λ

$$\left\langle \Psi \middle| \hat{H} \middle| \Phi \right\rangle = -\left\langle 0 \middle| c_\beta \sum_{a,b} \left\langle \varphi_a \middle| H \middle| \varphi_b \right\rangle c_a^\dagger c_b c_\lambda^\dagger \middle| 0 \right\rangle = -\left\langle 0 \middle| c_\beta \sum_a \left\langle \varphi_a \middle| H \middle| \varphi_\lambda \right\rangle c_a^\dagger \middle| 0 \right\rangle$$

$$= -\left\langle \varphi_\beta \middle| H \middle| \varphi_\lambda \right\rangle$$

- So we do get the correct sign!

Change of basis

$\left|\mu\right\rangle = c_\mu^\dagger \left|0\right\rangle$ Choose another basis: $\left|\tilde{\mu}\right\rangle = c_{\tilde{\mu}}^\dagger \left|0\right\rangle$

But

$$c_\mu^\dagger \left|0\right\rangle = \left|\mu\right\rangle = \sum_{\tilde{\mu}} \left\langle \tilde{\mu} \middle| \mu \right\rangle \left|\tilde{\mu}\right\rangle = \sum_{\tilde{\mu}} \left\langle \tilde{\mu} \middle| \mu \right\rangle c_{\tilde{\mu}}^\dagger \left|0\right\rangle$$

which means

$$c_\mu^\dagger = \sum_{\tilde{\mu}} \left\langle \tilde{\mu} \middle| \mu \right\rangle c_{\tilde{\mu}}^\dagger; \quad c_{\tilde{\mu}}^\dagger = \sum_{\mu} \left\langle \mu \middle| \tilde{\mu} \right\rangle c_\mu^\dagger;$$

$$c_\mu = \sum_{\tilde{\mu}} \left\langle \mu \middle| \tilde{\mu} \right\rangle c_{\tilde{\mu}}; \quad c_{\tilde{\mu}} = \sum_{\mu} \left\langle \mu \middle| \tilde{\mu} \right\rangle c_\mu$$

Strictly speaking, we cannot conclude that the operators are the same because they give the same result acting on the vacuum state (we should get the same result when they act on any state). But we can easily see that the equality holds give the structure of the Fock space. Alternatively, one can derive transformation rules of Slater determinants and show that they are compatible.

One-electron operators I

- We can use a change of basis to rederive our expression for the one-electron operator.
- Consider one-electron wave functions that diagonalize *H*, so that

$$H\left(\boldsymbol{r}\right)\varphi_{\lambda}\left(\boldsymbol{r}\right)=E_{\lambda}\varphi_{\lambda}\left(\boldsymbol{r}\right)$$

- Form a NxN Slater determinants with such functions, then it is very easy to show that

$$\left\langle \Psi\left|\hat{H}\right|\Phi\right\rangle =\delta_{\Psi,\Phi}\sum_{i=1}^{N}E_{\lambda_{i}}$$

One-electron operators II

- Now let's switch to the occ. number rep.

$$\Psi \Rightarrow \left| n_{\lambda_1}^{\Psi}, n_{\lambda_2}^{\Psi}, n_{\lambda_3}^{\Psi}, ... \right\rangle \quad \Phi \Rightarrow \left| n_{\lambda_1}^{\Phi}, n_{\lambda_2}^{\Phi}, n_{\lambda_3}^{\Phi}, ... \right\rangle$$

- and consider the operator

$$\sum_{i=1}^{N} E_{\lambda_i} c_{\lambda_i}^{\dagger} c_{\lambda_i} = \sum_{i=1}^{N} E_{\lambda_i} \hat{n}_{\lambda_i}$$

- then

$$\sum_{i=1}^{N} E_{\lambda_i} \hat{n}_{\lambda_i} \left| n_{\lambda_1}^{\Phi}, n_{\lambda_2}^{\Phi}, n_{\lambda_3}^{\Phi}, ... \right\rangle = \sum_{i=1}^{N} E_{\lambda_i} n_{\lambda_i}^{\Phi} \left| n_{\lambda_1}^{\Phi}, n_{\lambda_2}^{\Phi}, n_{\lambda_3}^{\Phi}, ... \right\rangle$$

- so

$$\left\langle \Psi \right| \sum_{i=1}^{N} E_{\lambda_i} \hat{n}_{\lambda_i} \left| n_{\lambda_1}^{\Phi}, n_{\lambda_2}^{\Phi}, n_{\lambda_3}^{\Phi}, ... \right\rangle = \delta_{\Psi,\Phi} \sum_{i=1}^{N} E_{\lambda_i}$$

One electron operators (III)

- Therefore

$$\hat{H} = \sum_{i=1}^{N} E_{\lambda_i} c_{\lambda_i}^{\dagger} c_{\lambda_i} = \sum_{i=1}^{N} \left\langle \lambda_i \middle| V \middle| \lambda_i \right\rangle c_{\lambda_i}^{\dagger} c_{\lambda_i}$$

Suppose now that we switch to another base

$$c_{\lambda_i}^{\dagger} = \sum_j \left\langle \mu_j \middle| \lambda_i \right\rangle c_{\mu_j}^{\dagger}; \quad c_{\lambda_i} = \sum_j \left\langle \lambda_i \middle| \mu_j \right\rangle c_{\mu_j}$$

$$\hat{H} = \sum_{i=1}^{N} E_{\lambda_i} c_{\lambda_i}^{\dagger} c_{\lambda_i} = \sum_{i=1}^{N} \left\langle \lambda_i \middle| H \middle| \lambda_i \right\rangle \sum_j \left\langle \mu_j \middle| \lambda_i \right\rangle c_{\mu_j}^{\dagger} \sum_{j'} \left\langle \lambda_i \middle| \mu_{j'} \right\rangle c_{\mu_{j'}}$$

$$= \sum_{jj'} c_{\mu_j}^{\dagger} c_{\mu_{j'}} \sum_i \left\langle \mu_j \middle| \lambda_i \right\rangle \left\langle \lambda_i \middle| H \middle| \lambda_i \right\rangle \left\langle \lambda_i \middle| \mu_{j'} \right\rangle$$

But we have show earlier, for a diagonal operator

$$H = \sum_{\lambda,\lambda'} \left\langle \lambda \middle| H \middle| \lambda' \right\rangle \left| \lambda \right\rangle \left\langle \lambda' \right| = \sum_{\lambda} \left\langle \lambda \middle| H \middle| \lambda \right\rangle \left| \lambda \right\rangle \left\langle \lambda \right|$$

One electron operators (IV)

- So

$$\hat{V} = \sum_{jj'} \left\langle \mu_j \middle| V \middle| \mu_{j'} \right\rangle c^{\dagger}_{\mu_j} c_{\mu_{j'}}$$

- Notice that the equation $\left\langle \Psi \middle| \hat{H} \middle| \Phi \right\rangle = \delta_{\Psi,\Phi} \sum_{i=1}^{N} E_{\lambda_i}$ would also be valid for symmetric wavefunctions, so the derivation here suggests that the one-electron operator expression is valid for bosons and fermions.

Tight binding hamiltonian (I)

- The atomic wave functions are $\phi_{aj,\boldsymbol{R}}\left(\boldsymbol{r}\right)$
- Therefore, the hamiltonian in second quantization is

$$H=\sum_{\substack{aj\boldsymbol{R}\\a'j'\boldsymbol{R}'}}\left\langle aj\boldsymbol{R}\right|H\left|a'j'\boldsymbol{R}'\right\rangle c_{aj\boldsymbol{R}}^{\dagger}c_{a'j'\boldsymbol{R}'}$$

- Now define

$$c_{aj\boldsymbol{k}}^{\dagger}=\frac{1}{\sqrt{N}}\sum_{\boldsymbol{R}}e^{i\boldsymbol{k}\cdot\left(\boldsymbol{R}+\boldsymbol{d}_{j}\right)}c_{aj\boldsymbol{R}}^{+}$$

- The inverse is

$$c_{aj\boldsymbol{R}}^{+}=\frac{1}{\sqrt{N}}\sum_{\boldsymbol{k}}e^{-i\boldsymbol{k}\cdot\left(\boldsymbol{R}+\boldsymbol{d}_{j}\right)}c_{aj\boldsymbol{k}}^{\dagger}$$

Tight binding hamiltonian (II)

- Therefore

$$H = \frac{1}{N}\sum_{\boldsymbol{k}\boldsymbol{k}'} c^{\dagger}_{aj\boldsymbol{k}} c_{a'j'\boldsymbol{k}'} \sum_{\substack{aj\boldsymbol{R} \\ a'j'\boldsymbol{R}'}} \left\langle aj\boldsymbol{R}\right| H \left|a'j'\boldsymbol{R}'\right\rangle e^{-i\boldsymbol{k}\cdot\left(\boldsymbol{R}+\boldsymbol{d}_j\right)} e^{i\boldsymbol{k}'\cdot\left(\boldsymbol{R}'+\boldsymbol{d}_{j'}\right)}$$

- Define $\boldsymbol{R}' = \boldsymbol{R} + \boldsymbol{S}$. Then

$$H = \frac{1}{N}\sum_{\boldsymbol{k}\boldsymbol{k}'} c^{\dagger}_{aj\boldsymbol{k}} c_{a'j'\boldsymbol{k}'} \sum_{\substack{aj\boldsymbol{R} \\ a'j'\boldsymbol{S}}} \left\langle aj\boldsymbol{R}\right| H \left|a'j'\boldsymbol{R}+\boldsymbol{S}\right\rangle e^{-i\boldsymbol{k}\cdot\boldsymbol{d}_j} e^{i\boldsymbol{k}'\cdot\left(\boldsymbol{S}+\boldsymbol{d}_{j'}\right)} e^{i\left(\boldsymbol{k}'-\boldsymbol{k}\right)\cdot\boldsymbol{R}}$$

- Because of translational symmetry

$$H = \frac{1}{N}\sum_{\boldsymbol{k}\boldsymbol{k}'} c^{\dagger}_{aj\boldsymbol{k}} c_{a'j'\boldsymbol{k}'} \sum_{\substack{aj \\ a'j'\boldsymbol{S}}} \left\langle aj\boldsymbol{0}\right| H \left|a'j'\boldsymbol{S}\right\rangle e^{-i\boldsymbol{k}\cdot\boldsymbol{d}_j} e^{i\boldsymbol{k}'\cdot\left(\boldsymbol{S}+\boldsymbol{d}_{j'}\right)} \sum_{\boldsymbol{R}} e^{i\left(\boldsymbol{k}'-\boldsymbol{k}\right)\cdot\boldsymbol{R}}$$

$$= \sum_{\boldsymbol{k}} c^{\dagger}_{aj\boldsymbol{k}} c_{a'j'\boldsymbol{k}} \sum_{\substack{aj \\ a'j'\boldsymbol{S}}} \left\langle aj\boldsymbol{0}\right| H \left|a'j'\boldsymbol{S}\right\rangle e^{i\boldsymbol{k}\cdot\left(\boldsymbol{S}+\boldsymbol{d}_{j'}-\boldsymbol{d}_j\right)} = \sum_{\substack{\boldsymbol{k} \\ aj \\ a'j'}} c^{\dagger}_{aj\boldsymbol{k}} c_{a'j'\boldsymbol{k}} H_{a'j',aj}\left(\boldsymbol{k}\right)$$

Tight binding hamiltonian (III)

- If we now diagonalize the matrix $H_{a'j',aj}\left(\boldsymbol{k}\right)$ we will find eigenstates $\left|n\boldsymbol{k}\right\rangle$
- We then define

$$c^{\dagger}_{aj\boldsymbol{k}} = \sum_{n}\left\langle n\boldsymbol{k}\middle| aj\boldsymbol{k}\right\rangle c^{\dagger}_{n\boldsymbol{k}}; \quad c_{aj\boldsymbol{k}} = \sum_{n}\left\langle aj\boldsymbol{k}\middle| n\boldsymbol{k}\right\rangle c_{n\boldsymbol{k}}$$

- and the hamiltonian becomes

$$H = \sum_{\boldsymbol{k}}\sum_{aj}\sum_{a'j'} c^{\dagger}_{aj\boldsymbol{k}} c_{a'j'\boldsymbol{k}} H_{a'j',aj}\left(\boldsymbol{k}\right) =$$

$$= \sum_{\boldsymbol{k}}\sum_{n,n'}\sum_{aj}\sum_{a'j'} c^{\dagger}_{n\boldsymbol{k}} c_{n'\boldsymbol{k}} \left\langle n\boldsymbol{k}\middle| aj\boldsymbol{k}\right\rangle H_{a'j',aj}\left(\boldsymbol{k}\right)\left\langle a'j'\boldsymbol{k}\middle| n'\boldsymbol{k}\right\rangle$$

$$= \sum_{\boldsymbol{k}}\sum_{n,n'} c^{\dagger}_{n\boldsymbol{k}} c_{n'\boldsymbol{k}} \left\langle n\boldsymbol{k}\middle| H\middle| n'\boldsymbol{k}\right\rangle = \sum_{\boldsymbol{k}}\sum_{n,n'} c^{\dagger}_{n\boldsymbol{k}} c_{n'\boldsymbol{k}} \varepsilon_{n\boldsymbol{k}}\delta_{n,n'} = \sum_{n\boldsymbol{k}} \varepsilon_{n\boldsymbol{k}} c^{\dagger}_{n\boldsymbol{k}} c_{n\boldsymbol{k}}$$