

### Warm-Up Questions:

#### 1.1)

a) Hartree Product:  $\psi_{HP} = \psi(r_1)\psi(r_2)$

b) Slater Determinant:  $\psi(x_1, x_2) = \frac{1}{\sqrt{2}} \det \begin{bmatrix} \psi_1(x_1) & \psi_2(x_1) \\ \psi_1(x_2) & \psi_2(x_2) \end{bmatrix} = \frac{1}{\sqrt{2}} [\psi_1(x_1)\psi_2(x_2) - \psi_1(x_2)\psi_2(x_1)]$

1.2) Assuming that  $\psi_1$  and  $\psi_2$  are orthogonal,

$$P(r_1, r_2) = \int \psi^*(x_1, x_2) \psi(x_1, x_2) dx_1 dx_2 = \frac{1}{2} \int (|\psi_1(x_1)|^2 |\psi_2(x_2)|^2 + |\psi_1(x_2)|^2 |\psi_2(x_1)|^2)$$

Now, we know from linear algebra that the determinant is invariant under row and column operations,

therefore, if we swap the particles, our new SD will be  $\psi(x_2, x_1) = \frac{1}{\sqrt{2}} \det \begin{bmatrix} \psi_2(x_1) & \psi_1(x_1) \\ \psi_2(x_2) & \psi_1(x_2) \end{bmatrix}$

Which is basically a swap between the matrix's two columns  $\Rightarrow$  has the same determinant as before.

Therefore our integrand will be the same and we'll get the same probability which means our particles are identical.

Instead of the Slater determinant, we could use the Slater permanent. (Use of a plus sign instead of a minus sign) Which equals:  $\frac{1}{\sqrt{2}} [\psi_1(x_1)\psi_2(x_2) + \psi_1(x_2)\psi_2(x_1)]$ , the permanent is also invariant under row and column operations, therefore it would result in the particles being identical once again.

In the case we use the determinant, our composite wavefunction is antisymmetric, whose particles we call a **fermion** and in the permanent case, the wavefunction is symmetric, which we'll call **bosons**.

1.3) Assuming we already know that the electron is a fermion and that spin and position are decoupled, we can write (c and d for spin coordinates)

$\chi_1 = \psi_1(x_1)c(w_1), \chi_1 = \psi_2(x_2)d(w_2)$ . The probability using the slater determinant will be (replacing  $\psi$ 's with  $\chi$ 's):

$$P(x_1, x_2) = \frac{1}{2} \int (|\psi_1(x_1)|^2 |\psi_2(x_2)|^2 |c(w_1)|^2 |d(w_2)|^2 + |\psi_1(x_2)|^2 |\psi_2(x_1)|^2 |c(w_1)|^2 |d(w_2)|^2 \\ + \psi_1(x_1)\psi_1^*(x_2)\psi_2(x_2)\psi_2^*(x_1)|c(w_1)d^*(w_2)|^2 \\ + \psi_1^*(x_1)\psi_1(x_2)\psi_2^*(x_2)\psi_2(x_1)|c(w_1)^*d(w_2)|^2)$$

If our electrons have the same spin (triplet state), the spin coefficients of the last two terms of the integrand will be 1, but if they have opposite signs (are orthogonal; singlet state), the coefficients will be 0 and we'll have no correlation cross-terms, therefore we will get the same probability that we'd get, had we used the Hartree product (which assumes that the particles are distinguishable). Which means that the slater determinant violates Pauli's exclusion principle, therefore it is not a good ansatz for our particles.

1.4) Knowing that  $\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2 \langle x_1 x_2 \rangle$ , for our identical particles we can write (Assuming orthogonality and normalization):

$$\psi_+(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_a(x_1)\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)];$$

For bosons:

$$\psi_{-}(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_a(x_1)\psi_b(x_2) - \psi_b(x_1)\psi_a(x_2)].$$

For fermions:

$$\begin{aligned} \langle x_1^2 \rangle &= \frac{1}{2} \left[ \int x_1^2 |\psi_a(x_1)|^2 dx_1 \int |\psi_b(x_2)|^2 dx_2 \right. \\ &\quad + \int x_1^2 |\psi_b(x_1)|^2 dx_1 \int |\psi_a(x_2)|^2 dx_2 \\ &\quad \pm \int x_1^2 \psi_a(x_1)^* \psi_b(x_1) dx_1 \int \psi_b(x_2)^* \psi_a(x_2) dx_2 \\ &\quad \left. \pm \int x_1^2 \psi_b(x_1)^* \psi_a(x_1) dx_1 \int \psi_a(x_2)^* \psi_b(x_2) dx_2 \right] \\ &= \frac{1}{2} [\langle x^2 \rangle_a + \langle x^2 \rangle_b \pm 0 \pm 0] = \frac{1}{2} (\langle x^2 \rangle_a + \langle x^2 \rangle_b). \end{aligned}$$

Similarly,

$$\langle x_2^2 \rangle = \frac{1}{2} (\langle x^2 \rangle_b + \langle x^2 \rangle_a).$$

(Naturally,  $\langle x_2^2 \rangle = \langle x_1^2 \rangle$ , since you can't tell them apart.) But

$$\begin{aligned} \langle x_1 x_2 \rangle &= \frac{1}{2} \left[ \int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)|^2 dx_2 \right. \\ &\quad + \int x_1 |\psi_b(x_1)|^2 dx_1 \int x_2 |\psi_a(x_2)|^2 dx_2 \\ &\quad \pm \int x_1 \psi_a(x_1)^* \psi_b(x_1) dx_1 \int x_2 \psi_b(x_2)^* \psi_a(x_2) dx_2 \\ &\quad \left. \pm \int x_1 \psi_b(x_1)^* \psi_a(x_1) dx_1 \int x_2 \psi_a(x_2)^* \psi_b(x_2) dx_2 \right] \\ &= \frac{1}{2} (\langle x \rangle_a \langle x \rangle_b + \langle x \rangle_b \langle x \rangle_a \pm \langle x \rangle_{ab} \langle x \rangle_{ba} \pm \langle x \rangle_{ba} \langle x \rangle_{ab}) \\ &= \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2, \end{aligned}$$

where

$$\langle x \rangle_{ab} \equiv \int x \psi_a(x)^* \psi_b(x) dx.$$

Thus

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

In the last equation, the plus sign on the left-hand side belongs to the bosons and the minus sign to the fermions. Knowing that this difference for identical particles is:

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

We realize that identical bosons are closer to each other and identical bosons are farther than each other compared to indistinguishable particles.

### Challenge Questions:

1)

Slater determinants capture the correlation terms between fermions in the triplet state.

- a) In the configuration interaction method, determinants of excited state orbitals (singly and doubly excited) are used, and in the coupled cluster method, even more than doubly excited determinants are used (applying different powers to normal orbitals and excited orbitals)
- b) We can encapsulate more electronic attributes relating to their interactions (coulomb interactions, spin-spin coupling, angular momentum interactions, etc) by creating additional determinants (sometimes even virtual orbitals!) and giving them the proper coefficients to normalize for the different strengths of the different interactions.
- c) If we try to solve the Schrodinger equation in the CI method exactly, then yes, the symmetries are conserved (which is computationally expensive), otherwise, there might be deviations. And in the CC method, if we try to use symmetry-adapted clusters, the symmetrical properties will be almost conserved, but we will have to introduce non-linear terms which might pose a problem when solving the equations.

2)

```
from qiskit import QuantumCircuit, ClassicalRegister, QuantumRegister

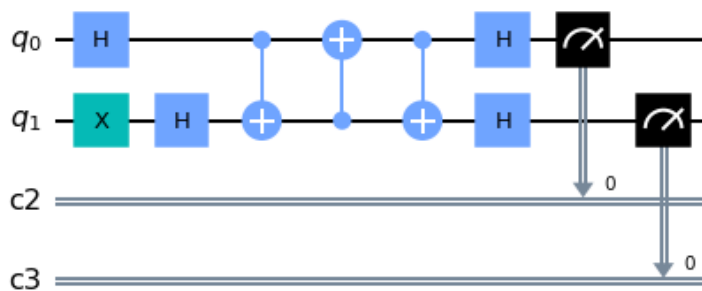
q = QuantumRegister(2, name="q")
c_a = ClassicalRegister(1)
c_b = ClassicalRegister(1)

circuit = QuantumCircuit(q, c_a, c_b)

circuit.h(q[0])
circuit.x(q[1])
circuit.h(q[1])
# SWAP
circuit.cx(q[0], q[1])
circuit.cx(q[1], q[0])
circuit.cx(q[0], q[1])
# end of SWAP
circuit.h(q[0])
circuit.h(q[1])

circuit.measure(q[0], c_a)
circuit.measure(q[1], c_b)

circuit.draw(output="mpl")
```



This is a quantum circuit, if we use spin of electrons as our qubits, it will be equivalent to a double-slit experiment.