

Worksheet 8B Solutions

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1. Consider the following definitions for electron wavefunctions:

- Spatial component:

$$1s(1) = \psi_{1s}(r_1) = \phi_{trial}(r_1) \quad (1)$$

- Spin component:

$$\alpha(1), \beta(1) \quad (2)$$

With the following known integrals:

- $\langle 1s(1)|1s(1)\rangle = 1$
- $\langle 1s(1)|1s(2)\rangle = 1$
- $\langle \alpha|\alpha\rangle = \langle \beta|\beta\rangle = 1$
- $\langle \alpha|\beta\rangle = 0$

Two possible spin orbitals:

$$\Psi_{100\frac{1}{2}} = 1s\alpha(1) \quad (3)$$

and

$$\Psi_{100-\frac{1}{2}} = 1s\beta(1) \quad (4)$$

Linear combinations:

- $\Psi_1 = 1s\alpha(1)1s\beta(2) + 1s\beta(1)1s\alpha(2)$
- $\Psi_2 = 1s\alpha(1)1s\beta(2) - 1s\beta(1)1s\alpha(2)$

- (a) Is $\Psi_{100-\frac{1}{2}} = 1s\alpha(1)$ an appropriate representation for an electron in an atom? Justify your answer.

Yes, $\Psi_{100-\frac{1}{2}} = 1s\alpha(1)$ is an allowed representation for an electron because it specifies all information, ie. all four quantum numbers. However, it is not a general wavefunction because it does not account for the possibility of $m_s = \frac{1}{2}$.

- (b) How can you combine $\Psi_{100\frac{1}{2}} = 1s\alpha(1)$ and $\Psi_{100-\frac{1}{2}} = 1s\beta(1)$ to make an appropriate representation for an electron in an atom?

We can form a linear combination of the basis states to form a general wavefunction: $\Psi_{general} = c_1 1s\alpha(1) + c_2 1s\beta(2)$

- (c) Electron wavefunctions must be totally antisymmetric with respect to the exchange of any two electrons. Do either $\Psi_1 = 1s\alpha(1)1s\beta(2) + 1s\beta(1)1s\alpha(2)$ or $\Psi_2 = 1s\alpha(1)1s\beta(2) - 1s\beta(1)1s\alpha(2)$ satisfy the antisymmetry requirement for electron wavefunctions?

$\Psi_2 = 1s\alpha(1)1s\beta(2) - 1s\beta(1)1s\alpha(2)$ satisfies the antisymmetry requirement when we switch the place of each 1 and 2 in the expression.

2. (a) One way to ensure antisymmetry enlists a *Slater determinant*. What is the value of the determinant, $\Psi(1, 2) = \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix}$?

Evaluating it, we obtain:

$$\Psi(1, 2) = \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix} = 1s\alpha(1)1s\beta(2) - 1s\beta(1)1s\alpha(2) \quad (5)$$

(b) What happens to the determinant when we switch rows?

We obtain:

$$\Psi(2, 1) = \begin{vmatrix} 1s\alpha(2) & 1s\beta(2) \\ 1s\alpha(1) & 1s\beta(1) \end{vmatrix} = 1s\beta(1)1s\alpha(2) - 1s\alpha(1)1s\beta(2) = -\Psi(1, 2) \quad (6)$$

(c) Are $\Psi(1, 2)$ and $\Psi(2, 1)$ normalized? If not, what is the normalization constant?

If we evaluate the inner products of each wavefunction, we'll find that they each result in 2, so they are not normalized. To normalize them, we would use a factor of $N = \frac{1}{\sqrt{2}}$.

3. The Slater determinant can be generalized to as many electrons as needed:

$$\Psi(1, 2, \dots, N) = \begin{vmatrix} \mu_1(1) & \mu_2(1) & \cdots & \mu_N(1) \\ \mu_1(2) & \mu_2(2) & \cdots & \mu_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \mu_1(N) & \mu_2(N) & \cdots & \mu_N(N) \end{vmatrix} \quad (7)$$

where μ_{ij} is the i th orthonormal spin orbital of the j th electron.

What happens if two of the spin orbitals are identical?

If two of the spin orbitals are identical, we'll have two equal rows in the determinant. Upon exchange of any two rows, according to the properties of a determinant, its value should negative its former value. However, since the exchanged rows are equivalent, the value should also be unchanged. The only value equal to itself and its negative is zero. This is a state