Model 0 - Observables and Expectation Values: Recall the following postulates from the previous Worksheet:

**Postulate II.** Every dynamical variable (or physical observable) is represented by a corresponding linear operator.

**Postulate III.** When a dynamical variable \( A \) is measured (without experimental error), there are only certain possible values that may be obtained. These values are the eigenvalues \( a_i \) of the operator \( \hat{A} \) as given by

\[
\hat{A}\phi_i = a_i\phi_i
\]

where \( \phi_i \) is one of the eigenfunctions of the operator \( \hat{A} \) representing the dynamical variable \( A \).

When a system is not in an eigenstate of the observable \( A \) of interest, it is possible to say much more than simply the result of a measurement must be one of the eigenvalues of the operator \( \hat{A} \). It is a property of observable operators \( \hat{A} \) that the set of all eigenfunctions of such an operator \( \{\phi(\tau)\} \) forms a complete basis set with which any wavefunction in of the system \( \psi(\tau) \) may be expanded:

\[
\psi(\tau) = \sum_i c_i\phi_i(\tau) \quad (0-1)
\]

“\( \tau \)” here denotes all of the coordinates of the system. The coefficients \( c_i \) in expansion 0-1 provide the relative probabilities \( P(\phi) \) that a measurement of \( A \) will find the system in the eigenstate \( \phi_i \) and the measurement of \( A \) will therefore yield the value \( a_i \) in the following manner:

\[
P(\phi_i) = \frac{c_i^*c_i}{\int \psi^*(\tau)\psi(\tau)d\tau} \quad (0-2)
\]

If a measurement is made on a collection of systems all in the state \( \psi(\tau) \) the average or expectation value of the observable \( A \) is given by:

\[
< A >= \sum_i P(\phi_i)a_i = \frac{\int \psi^*(\tau)\hat{A}\psi(\tau)d\tau}{\int \psi^*(\tau)\psi(\tau)d\tau} \quad (0-3)
\]

(Note that if \( \psi \) is properly normalized \( \int \psi^*\psi d\tau = 1 \) and Eqs. 0-2 and 0-3 simplify accordingly.)
The Hydrogen Atom (II)
(What Else Do We Know About Hydrogen?)

We have seen that the electronic energies of the hydrogen atoms are quantized and that the single electron can occupy regions of space called orbitals. Now, we turn our attention to the angular momentum of the single electron in the atom, the probability of finding the electron at various locations in space, and the transition energy between different energy states.
Model 1: Eigenfunctions and Eigenvalues.

For the hydrogen atom model:

\[ \hat{H} \Psi_{n\ell m} = -\frac{\hbar^2}{2m_0a_0^2} \frac{1}{n^2} \Psi_{n\ell m} \]  \hspace{1cm} (1)

\[ \hat{L}^2 \Psi_{n\ell m} = \ell(\ell + 1) \hbar^2 \Psi_{n\ell m} \]  \hspace{1cm} (2)

\[ \hat{L}_z \Psi_{n\ell m} = m\hbar \Psi_{n\ell m} \]  \hspace{1cm} (3)

Note that in all three of these equations, when the operator is applied to the function (in this case, \( \Psi_{n\ell m} \)), the result is a constant multiplied by the original function. Equations of this type are referred to as eigenvalue equations, and the resulting constant is called an eigenvalue of the operator. Any function for which the equation is valid is an eigenfunction of the operator.

If the wavefunction \( \Psi_{n\ell m} \) is an eigenfunction of a particular operator, then the state of the system described by the wavefunction has a definite value for the physical property represented by the operator. For example, since \( \Psi_{n\ell m} \) is an eigenfunction of the total energy operator \( \hat{H} \), we say that the state described by the wavefunction \( \Psi_{n\ell m} \) has a definite total energy, and it is given by the eigenvalue:

\[ -\frac{\hbar^2}{2m_0a_0^2} \frac{1}{n^2} \]

If \( \Psi_{n\ell m} \) is not an eigenfunction of a particular operator (that is, when the operator is applied to \( \Psi_{n\ell m} \), the result is not a constant multiplied by \( \Psi_{n\ell m} \)), then the physical property associated with the operator does not have a definite value for the state described by \( \Psi_{n\ell m} \).  

Critical Thinking Questions

1. a) What are the \( n, \ell, \) and \( m \) values for \( \Psi_{100} \) of the hydrogen atom?

b) What is the value of the square of the angular momentum, \( L^2 \), for \( \Psi_{100} \) of the hydrogen atom? Recall that the value of Planck's constant bar, \( \hbar \), is \( 1.055 \times 10^{-34} \) Js.

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3Nonetheless, as we have seen previously, an average value for the physical property \( q \), \( \langle q \rangle \) can be obtained.
2. a) What are the $n$, $\ell$, and $m$ values for $\Psi_{210}$ of the hydrogen atom?

b) What is the value of the square of the angular momentum, $L^2$, for $\Psi_{210}$ of the hydrogen atom?

3. For a given $\Psi_{n\ell m}$ of the hydrogen atom does the square of the angular momentum, $L^2$, have a definite value? If so, what is it? You may give your answer in terms of $\hbar^2$ such as: $5\hbar^2$ or $n^2\hbar^2$.

4. For a given $\Psi_{n\ell m}$ of the hydrogen atom does the $z$-component of the angular momentum, $L_z$, have a definite value? If so, what is it? You may give your answer in terms of $\hbar$ such as: $5\hbar$ or $n^2\hbar$.

5. What is the value (eigenvalue) of $L_z$ for the wavefunction $\Psi_{2,1,-1}$? You may give your answer in terms of $\hbar$ such as: $5\hbar$ or $n^2\hbar$.

6. What is the value of $L^2$ for the wavefunction $\Psi_{2,1,-1}$? You may give your answer in terms of $\hbar^2$ such as: $5\hbar^2$ or $n^2\hbar^2$.

7. What is the expression for the magnitude of $L$, $|L|$, for the wavefunction $\Psi_{n\ell m}$?
8. What is the value of the magnitude of $L$, $|L|$, for the wavefunction $\Psi_{2,1,-1}$? You may give your answer in terms of $\hbar$ such as: $5\hbar$ or $n^2\hbar$.

9. In order for equations (2) and (3) to be reasonable, it must be the case that the $z$-component of the angular momentum is smaller than or equal to the magnitude of the angular momentum. Expressed algebraically, $L_z \leq |L|$.

   a) Use a vector diagram (for the angular momentum and for the $z$-component of the angular momentum) to explain why this must be true in general (without reference to equations (2) and (3)).

   b) Show that this is true using equations (2) and (3) and the restriction on $n$, $\ell$, and $m$:

   $n = 0, 1, 2, ...$
   $\ell = 0, 1, 2, ... , n-1$
   $m = 0, \pm 1, \pm 2, ... , \pm \ell$
Exercises

1. An electron of a hydrogen atom is described by \( n = 4, \ell = 3, \) and \( m = -2, \Psi_{4,3,-2}. \)
   a) What is the energy, in joules?  b) What is the value of the magnitude of the angular momentum, \( L? \)  c) What is the value of the \( z \) component of the angular momentum, \( L_z? \)

2. Deduce the value of the magnitude of the total angular momentum, \( L, \) for any \( p \) orbital. For any \( d \) orbital.

3. Show that equations (2) and (3) are correct for \( \Psi_{100} \).

4. Show, explicitly, that \( \hat{L}_z \Psi_{n\ell m} = m\hbar \Psi_{n\ell m}. \)

5. Show that equation (2) is correct for \( \Psi_{210}. \)

6. What is the value of \( L^2 \) for the wavefunction \( \Psi_{4,3,1}? \) You may give your answer in terms of \( \hbar^2. \)

7. The operator for the position of the electron is \( \hat{r} = r. \) Is \( \Psi_{100} \) an eigenfunction of \( \hat{r} \)? If so, what is the eigenvalue? If not, what does this suggest about the position of the electron? [Hint: Here, \( r \) is the vector indicating the position in space of the electron: \( (r, \theta, \phi) \) or \( (x, y, z). \) Because \( \Psi_{100} \) depends only on the magnitude of \( r, \) the operator may be thought of as "multiply by \( r".\)\]

We have seen that the wavefunction $\Psi_{100}$ is not an eigenfunction of the position operator $\hat{\mathbf{r}}$. This result can be shown to be true for all of the hydrogen atom wavefunctions $\Psi_{n\ell m}$. Rather, the position of the electron in $\Psi_{n\ell m}$ is interpreted in a probabilistic manner. The probability of finding the electron between $r_i$ and $r_j$, $\theta_i$ and $\theta_j$, and $\phi_i$ and $\phi_j$ is given by:

$$P_{r,\theta,\phi} = \int_{r_i}^{r_j} \int_{\theta_i}^{\theta_j} \int_{\phi_i}^{\phi_j} \Psi^2 \ d\tau = \int_{r_i}^{r_j} \int_{\theta_i}^{\theta_j} \int_{\phi_i}^{\phi_j} R^2 \Theta^2 \Phi^2 \ d\tau$$  \hspace{1cm} (4)$$

where $d\tau$ is the volume element in spherical coordinates,

$$d\tau = r^2 \sin \theta \ d\theta \ d\phi \ dr$$  \hspace{1cm} (5)$$

$$P_{r,\theta,\phi} = \int_{r_i}^{r_j} \int_{\theta_i}^{\theta_j} \int_{\phi_i}^{\phi_j} R^2 \Theta^2 \Phi^2 \ r^2 \sin \theta \ d\theta \ d\phi \ dr$$  \hspace{1cm} (6)$$

Integration over all values of $\theta$ (0 to $\pi$) and all values of $\phi$ (0 to $2\pi$) yields the probability of finding the electron between $r_i$ and $r_j$:

$$P_r = \int_{r_i}^{r_j} r^2 \ R^2 \ dr$$  \hspace{1cm} (7)$$

The function $r^2 \ R^2$ is called the radial distribution function. This function is defined as the probability per unit value of $r$ of finding the electron at a distance $r$ from the nucleus. That is,

$$r^2 \ R^2 \ dr = \text{The probability that the particle lies at a distance from the nucleus between } r \text{ and } r + dr$$
Figure 1. The radial distribution function for the 1s, 2s and 2p orbitals.

This function can be used to determine the most probable distance of the electron from the nucleus. For \( \Psi'_{100} \), the most probable distance of the electron from the nucleus, \( r_{mp} \), can be shown to be:

\[
r_{mp} = a_o
\]

Critical Thinking Questions

10. Use equation (7) to write an expression that, when evaluated, will yield the value of the probability of finding the electron between \( r = a_o \) and \( r = 2a_o \).

11. Use equation (7) to write an expression which shows that the probability of finding the electron somewhere in the universe is 1.
12. Describe, using grammatically correct English sentences, how equation (8) can be obtained from the radial distribution function.

**Exercises**

8. Show how equation (7) is obtained from equation (6).

9. Carefully set up the integral that when evaluated will yield the probability of finding the electron in $\Psi_{100}$ of the hydrogen atom at $r$ values between $r = 0$ and $r = r_{mp}$. You may start with equation (7).

10. Recall that

$$\Psi_{2pz} = \frac{1}{4(2\pi)^{1/2}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r \cos \theta}{a_0} e^{-r/2a_0}.$$  

Carefully set up the integral in terms of $r$, $\theta$, and $\phi$, that will, when evaluated, give the probability of finding an electron in a $2p_z$ orbital at locations where $r \leq a_0$ and $x$, $y$, and $z$ are positive—as shown in the figure below.

11. Show explicitly how equation (8) can be obtained for a $1s$ orbital.

12. Calculate the average value of $r$, $<r>$, for $\Psi_{100}$. Compare this value to $r_{mp}$ and rationalize the result based on the representation of $r^2R^2$ for $\Psi_{100}$ in Figure 1.
Multielectron Atoms
(Why does life have to be so complicated?)

Fortunately, there are atoms with more than one electron, multielectron atoms. Even hydrogen can have more than one electron—the hydride ion. If there weren't multielectron atoms, we would not exist. The theoretical explanation of the energies and the properties of these atoms has proven to be a formidable task for scientists. We will begin with the simplest multielectron atom—He.

Physical Chemistry
A Guided Inquiry

Atoms, Molecules, and Spectroscopy

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Information

As a shorthand notation for writing more complicated Schrödinger equations, we make the following definition:

\[ \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \]  

The Laplacian operator, \( \nabla^2 \), is read "del-squared".

Model 1: The Helium Atom.

\[ U = \frac{1}{2} m_e v_1^2 + \frac{1}{2} m_e v_2^2 + \frac{(2e)(-e)/4\pi\varepsilon_0}{r_1} + \frac{(2e)(-e)/4\pi\varepsilon_0}{r_2} + \frac{(-e)(-e)/4\pi\varepsilon_0}{r_{12}} \]

\[ U = \frac{1}{2} m_e v_1^2 + \frac{1}{2} m_e v_2^2 - \frac{2e^2/4\pi\varepsilon_0}{r_1} - \frac{2e^2/4\pi\varepsilon_0}{r_2} + \frac{e^2/4\pi\varepsilon_0}{r_{12}} \]  

\[ \hat{H}\Psi = \left( \frac{\hbar^2}{2m_e} (\nabla_1^2 + \nabla_2^2) - \frac{Ze^2/4\pi\varepsilon_0}{r_1} - \frac{Ze^2/4\pi\varepsilon_0}{r_2} + \frac{e^2/4\pi\varepsilon_0}{r_{12}} \right) \Psi = \varepsilon\Psi \]  

Equation (3) provides a general expression for any two-electron species, for example He, Li\(^+\), Be\(^{2+}\), etc.

Critical Thinking Questions

1. The velocities \( v_1 \) and \( v_2 \) are labeled separately in equation (2). Why isn't the mass of the electron labeled \( m_{e1} \) and \( m_{e2} \)?
2. There is a "2e^2" in the third and fourth terms of the right-hand-side of equation (2). Why is there no "2e^2" in the fifth term?

3. There is a negative sign in front of the third and fourth terms of equation (2). Why? Why is there a positive sign in front of the fifth term?

4. What does the Z represent in equation (3)? What is the value of Z for He? Li+? Be^{2+}?

Information

Mathematicians, chemists, physicists, and other industrious individuals have tried to find a function which is a solution to equation (3). None has succeeded. The reason for this is that this equation cannot be solved. There are no functions which are eigenfunctions of the Hamiltonian operator in equation (3).

Critical Thinking Question

5. Is this course over?
Information

For all atomic and molecular species with more than one electron, the Schrödinger equation cannot be solved. However, it is possible to generate functions which are approximate solutions. The variational method is one of the approximation methods used when the solution to the Schrödinger equation cannot be found, as is usually the case. The variational method is summarized below:

- Write the Hamiltonian in the usual fashion and write \( \hat{H} \Psi = \varepsilon \Psi \).
- If the Schrödinger equation cannot be solved, make an educated guess—called the trial solution, \( \Psi_{\text{trial}} \). (The trial solution must obey the boundary conditions.)
- Determine the average value of \( \varepsilon \).

\[
<\varepsilon> = \frac{\int \Psi_{\text{trial}}^* \hat{H} \Psi_{\text{trial}} d\tau}{\int \Psi_{\text{trial}}^* \Psi_{\text{trial}} d\tau} \tag{4}
\]

It can be shown that the average value of the energy will be too high when this equation is used for the average value of the energy. That is, the true energy of the system is always lower than the value calculated with equation (4).

- If necessary, make another educated guess for \( \Psi_{\text{trial}} \) and recalculate the average value for the energy.
- The lower the energy of the trial solution, the closer the trial solution is to the real solution of the Schrödinger equation. (Remember, it is not possible to find a trial solution that yields an energy lower than the actual energy of the system.)

Model 2: Trial Function for a Particle-on-a-Line.

\[
\begin{align*}
\hat{H} \Psi &= \frac{-\hbar^2}{8m\pi^2} \frac{d^2 \Psi}{dx^2} = \varepsilon \Psi \tag{5} \\
\Psi_{\text{trial}} &= B \left[ x(a - x) \right] \tag{6} \\
<\varepsilon> &= \frac{10}{\pi^2 8ma^2} \frac{\hbar^2}{8} \tag{7}
\end{align*}
\]
Critical Thinking Questions

6. The boundary condition for a particle-on-a-line is that \( \Psi = 0 \) at \( x = 0 \) and \( \Psi = 0 \) at \( x = a \). Does the trial function obey the boundary condition?

7. Compare the average value of the energy, equation (7), with the actual solution of the Schrödinger equation \( (n_x = 1) \):

\[
\epsilon = \frac{\hbar^2}{8ma^2}
\]

Which yields the lower energy? Is this consistent with the variational principle—the principle that it is not possible for the calculated energy to be lower than the true energy for the system?

Exercises

1. Use the trial function (6) in Model 2 and the variational principle to obtain the value of <\( \epsilon \)> given in equation (7).

2. Calculate the energy, in joules, for the particle-on-a-line with the trial function in Model 2 and with the actual solution to the Schrödinger equation; let the length of the line = 1000 nm. Express the difference in the energy as a percent. Would you characterize \( \Psi_{\text{trial}} \) as: a good guess; a bad guess; an OK guess? Can you make a better guess?

Model 3: Trial Function for the Helium Atom.

- The Schrödinger equation cannot be solved for the helium atom.

- \( \text{He}^{2+}(g) + 2 \text{e}^- = \text{He}(g) \quad \Delta U_{\text{experimental}} = -7,621 \text{ kJ/mole} \) \quad (8)

We use a trial function that has each electron in a \( 1s \) orbital.

\[
\Psi_{\text{trial}} = \Psi_{\text{trial}(1)}\Psi_{\text{trial}(2)} = \Psi_{1s}(1) \Psi_{1s}(2) = \frac{1}{\pi} \left( \frac{Z}{a_0} \right)^3 e^{-Zr_1/a_0} e^{-Zr_2/a_0}
\]

where 1 and 2 refer to electron 1 and electron 2, respectively.
Critical Thinking Questions

8. The boundary condition for the electrons in an atom is that \( \Psi \) approaches zero as \( r \) approaches infinity. Does the trial function of Model 3 obey this boundary condition?

9. Provide a rationale for using the wave functions of the hydrogen atom as trial functions for the helium atom.

10. The trial probability function for electron 1 is \( \Psi_{1s}^2(1) \). The trial probability function for electron 2 is \( \Psi_{1s}^2(2) \). Suggest a reason why the full trial function is \( \Psi_{1s}(1)\Psi_{1s}(2) \) and not \( \Psi_{1s}(1) + \Psi_{1s}(2) \).

Information

Note that it is possible to use the trial function (9) to calculate the average energy using different values for \( Z \). Some results are shown in Table 1.

<table>
<thead>
<tr>
<th>( Z )</th>
<th>Energy (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.25</td>
<td>-6644</td>
</tr>
<tr>
<td>2.00</td>
<td>-7218</td>
</tr>
<tr>
<td>1.75</td>
<td>-7464</td>
</tr>
<tr>
<td>1.50</td>
<td>-7382</td>
</tr>
<tr>
<td>1.25</td>
<td>-6972</td>
</tr>
</tbody>
</table>
Critical Thinking Questions

11. Which value of $Z$ in Table 1 provides a function which is the best approximation to the ground state of the He atom? What is the basis for your answer?

12. What physical explanation can you provide for the result that the "best" value of $Z$ is NOT $Z = 2$?

Information

If $Z$, in Model 3, is treated as a variable, $Z'$, the average energy for helium can be determined as a function of $Z'$: $\epsilon(\text{He}) = f(Z')$. The lowest energy can be minimized by setting the derivative of $\langle \epsilon \rangle$ with respect to $Z'$ equal to zero and solving for the value of $Z'$.

$$\frac{d \langle \epsilon \rangle}{dZ'} = 0$$

The energy is minimized when $Z' = 27/16$; $\langle \epsilon \rangle = -7,475$ kJ/mole.

Exercises

3. When the parameter for the effective nuclear charge, $Z'$, is used in equation (4), the following expression for the average value of the energy, $\langle \epsilon \rangle$, is obtained:

$$\langle \epsilon \rangle = (Z')^2 - 4Z' + \frac{5}{8}Z'$$

where $Z'$ is the effective nuclear charge and the units are Hartree's, $H$. $H = 4.3597 \times 10^{-21}$ kJ.

(a) Show that application of the variational principle to this expression for $\langle \epsilon \rangle$ yields $Z' = 27/16$.

(b) Show that the energy calculated with this expression yields the value given above, $-7,475$ kJ/mole.
Model 4: Helium: Effective Nuclear Charge and Screening.

Critical Thinking Questions

13. a) What is the experimental value for the electronic energy of He?

b) Are the average energies for the $Ψ_{trial}$ with $Z' = 2$ and for the $Ψ_{trial}$ with $Z' = 27/16$ higher or lower than the experimental electronic energy of helium?

14. Which is the better trial function for the helium atom: $Ψ_{trial}$ with $Z' = 2$ or $Ψ_{trial}$ with $Z' = 27/16$? Explain.

15. According to the figure in Model 4, electron 2 is closer to the nucleus than electron 1. In this configuration, electron 2 is said to screen the nuclear charge on electron 1. In models 1 and 2 both electrons are in a $1s$ orbital. Do you think that electron 1 can screen the nuclear charge from electron 2?

16. Provide a rationale in terms of the physical system for why the trial with $Z' = 27/16$ gives a better energy value than when $Z' = 2$. 
Information

- An alternative to the use of the term screening is the term effective nuclear charge. For He, the effective nuclear charge is 27/16.

- Even better values for the energy of He can be calculated by using trial functions that have more parameters. A trial function with 2000 parameters yields an energy value that is within the experimentally determined value for helium.

Model 5: Lithium.

- The Schrödinger equation cannot be solved for the lithium atom.

- It has been determined from photoelectron spectroscopy (PES) that two of the three electrons are at the same energy level and the third electron is at a different (and higher) energy level. [Recall that PES measures the ionization energies of electrons in atoms (and molecules).]

\[ \Psi_{\text{trial}} = \Psi_{\text{trial}(1)}\Psi_{\text{trial}(2)}\Psi_{\text{trial}(3)} = \Psi_{1s(1)}\Psi_{1s(2)}\Psi_{2s(3)} \]  

where 1, 2, and 3 refer to electron 1, electron 2, and electron 3, respectively.

Critical Thinking Questions

17. How many kinetic energy terms are present in the expression for the classical electronic energy of lithium? Hint, see equation (3) for helium.

18. How many attractive Coulombic energy terms are present in the expression for the classical electronic energy of lithium?

19. How many repulsive Coulombic energy terms are present in the expression for the classical electronic energy of lithium?
20. Write the Hamiltonian operator for lithium. Hint: see equation (3).

**Model 6: Lithium: Effective Nuclear Charge and Screening.**

Critical Thinking Questions

21. When the electrons are arranged as in Model 6, electron 2 is closer to the nucleus than electron 3. In this configuration, electron 2 is said to *screen* the nuclear charge on electron 3. Sketch a similar diagram in which electron 2 screens electron 1.

22. Sketch a diagram in which electron 3 screens electron 1 and/or electron 2.
23. Based on the trial function (eq. 10) and your current understanding of the electronic structure of Li, explain why this configuration is less likely than the previous two.

24. Comment on the validity of this statement: To some extent, every electron shields the nuclear charge from every other electron.

25. The probability functions of $\psi_{2s}$ and $\psi_{2p}$ for an electron in a hydrogen atom are shown below. Recall that Coulomb's law is inversely proportional to distance. If electrons are present in $\Psi_{1s}$, as they are in lithium, provide a rationale for why an electron in a $2p$ orbital is more shielded from the nuclear charge than an electron in a $2s$ orbital.
26. According to your answer above, which is the lower-energy electron configuration in lithium, $1s^22s^1$ or $1s^22p^1$? Explain why the ground state of lithium is $\Psi_{1s}(1)\Psi_{1s}(2)\Psi_{2s}(3)$ and not $\Psi_{1s}(1)\Psi_{1s}(2)\Psi_{2p}(3)$.

Exercises

4. Write the expression for the classical electronic energy of a Be atom. Write the Hamiltonian operator for a Be atom. Write a trial function for the electrons in a Be atom.

5. How many electron-electron repulsion terms are found in the Hamiltonian for the carbon atom? For the gold atom?

6. Write a trial function for the carbon atom. [Hint: see equation 10.]