3.012 Bonding-Structure: Questions/Answers

1 Quantum States and Wavefunctions

1.1 Dealing with Wavefunctions

- *How eigenfunctions are used in the Schrödinger equation (SE)?*

  In quantum mechanics, the state of a particle is described by a wavefunction. The time-dependent Schrödinger equation (TDSE) is used to determine the time-evolution of the wavefunction. When the potential V does not depend on time, we use the stationary Schrödinger equation (SSE) to calculate the eigenfunctions (=eigenstates) and the eigenenergies of a particle in the presence of the potential V. From these eigenergies and eigenfunctions, we can determine emission/adsorption energies, obtain the probability of finding the particle in a given spatial region, calculate expectations values, among others.

- *What are some ways in which we can apply the wavefunction to obtain probabilities?*

  In 1D, the probability of finding an electron (wavefunction=$\psi(x)$) in the spatial interval $x_{min} < x < x_{max}$ is given by the integral $\int_{x_{min}}^{x_{max}} \psi^*(x)\psi(x)dx$ (ψ must be normalized).

  In 3D, the probability of finding an electron (wavefunction=$\psi(\overrightarrow{r})$) in the spatial region Ω is given by $\int_{\Omega} \psi^*(\overrightarrow{r})\psi(\overrightarrow{r})d\overrightarrow{r}$

1.2 Quantization of the Energy

- *What exactly is the* Farbe (color) *Defect?*

  In Lecture 2, it was shown that a negative ion vacancy in ionic crystals can be assimilated to a 3-dimensional box able to trap an electron. The energies of the bound electron are quantized; the resulting adsorption/emission spectrum is discrete. Due to this color selectivity, the ion vacancy appears colored (hence the naming).

1.3 Quantum Interference

- *How does quantum interference work?*

  Due to the wave-like behavior of quantum particles, it is possible to create constructive/destructive interference between quantum states by linear superposition of wavefunctions (refer, for example, to Lecture 1 $\rightarrow$ electron diffraction/double-slit experiment).

2 Schrödinger Equation, Separation of Variables

2.1 Dealing with the Schrödinger Equation

- *Will we be needing to calculate with imaginary numbers in the wave equations?*

  Yes, it can happen. The imaginary part of a wavefunction is as important as it real part.

- *Which aspects of the SE do I need to know?*

  I am confused at the extent to which we need to know how to solve the SE.

  Among others, you need to be able to:

  - distinguish clearly between the TSDE and the SSE,

  - use the method of separation of variables,

  - solve the free particle, the particule in an infinite multi-dimensional box completely,

  - describe qualitatively the eigenfunctions (oscillation/exponential decay) and eigenvalues (discrete/continuous spectrum) for a particle in a step potential and a particle in a finite box,

  - explain how to solve the hydrogen-like atom and describe the eigenstates and eigenenergies,

  - discuss multi-electron atoms.

- *How do I know when to use the different versions of the SE?*

  We use the TDSE when the potential is time-dependent. The SSE is used otherwise. For the problems seen in class, the potential was always independent on time: $V = V(\vec{r})$.

2.2 Separation of Variables

- *Why can separation of variables be used in the 3 following situations: time-independent potential, particle in a multi-dimensional box, particle in a central potential?*

For the time-independent potential, the wavefunction $\Psi(\overrightarrow{r}, t)$ can be separated as $\Psi(\overrightarrow{r}, t) = \psi(\overrightarrow{r})f(t)$ because the potential does not depend on t; this expression is then injected in the TDSE. Similarly, to solve the SSE associated to a central potential, the wavefunction $\psi(\overrightarrow{r})$ is separated as $\psi(\overrightarrow{r}) = R(r)Y(\theta, \phi)$ because $V(r)$ does not depend on θ and ϕ.

For a particle in a multi-dimensional box, separation of variables works because the 3 spatial directions x, y and z are "equivalent" and "independent" [1].

- *It would be nice to have a bit more of the math on separation of variables.*

(1) <u>time-independent potential</u>

After substituting $\Psi(\overrightarrow{r}, t) = \psi(\overrightarrow{r})f(t)$ in the TDSE, one obtains:

$-\frac{\hbar^2}{2m}f(t)\nabla^2\psi(\overrightarrow{r}) + V(\overrightarrow{r})f(t)\psi(\overrightarrow{r}) = i\hbar\psi(\overrightarrow{r})\frac{\partial}{\partial t}f(t)$.

Dividing by $\psi(\overrightarrow{r})f(t)$:

$\frac{1}{\psi(\overrightarrow{r})}\left\{-\frac{\hbar^2}{2m}\nabla^2\psi(\overrightarrow{r}) + V(\overrightarrow{r})\psi(\overrightarrow{r})\right\} = i\hbar\frac{1}{f(t)}\frac{\partial}{\partial t}f(t)$.

A t-dependent function cannot equal a $\overrightarrow{r}$-dependent function unless these functions are equal to the same constant E. Thus:

$\frac{1}{\psi(\overrightarrow{r})}\left\{-\frac{\hbar^2}{2m}\nabla^2\psi(\overrightarrow{r}) + V(\overrightarrow{r})\psi(\overrightarrow{r})\right\} = E$ and $i\hbar\frac{1}{f(t)}\frac{\partial}{\partial t}f(t) = E$

The first equation gives the SSE from which $\psi(\overrightarrow{r})$ can be determined. From the second equation $(i\hbar\frac{\partial}{\partial t}f(t) = Ef(t))$ the time-depedent part $f(t)$ can be calculated $(f(t) \propto e^{-iEt/\hbar})$

(2) <u>multi-dimensional box</u>

The SSE for a multi-dimensional box is

$-\frac{\hbar^2}{2m}\nabla^2\psi(x, y, z) = E\psi(x, y, z)$

With the *ansatz* $\psi(x, y, z) = X(x)Y(y)Z(z)$, we obtain:

$-\frac{\hbar^2}{2m}\left\{YZ\frac{d^2X}{dx^2} + XZ\frac{d^2Y}{dy^2} + XY\frac{d^2Z}{dz^2}\right\} = EX(x)Y(y)Z(z)$.

Dividing by $X(x)Y(y)Z(z)$, we obtain:

$-\frac{\hbar^2}{2m}\left\{\frac{1}{X(x)}\frac{d^2X}{dx^2} + \frac{1}{Y(y)}\frac{d^2Y}{dy^2} + \frac{1}{Z(z)}\frac{d^2Z}{dz^2}\right\} = E$

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[1] The true mathematical reason is that the potential $V(x, y, z) = \begin{cases} 0 & \text{inside the box} \\ +\infty & \text{outside} \end{cases}$ can be written as the sum of three potentials $V_x(x) + V_y(y) + V_z(z)$ where: $V_x(x) = \begin{cases} 0 & \text{if } 0 < x < a \\ +\infty & \text{if } x < 0 \text{ or } a < x \end{cases}$, $V_y(y) = \begin{cases} 0 & \text{if } 0 < y < b \\ +\infty & \text{if } y < 0 \text{ or } b < y \end{cases}$, $V_z(z) = \begin{cases} 0 & \text{if } 0 < z < c \\ +\infty & \text{if } z < 0 \text{ or } c < z \end{cases}$.

A sum of functions of independent variables can not be equal to a constant unless the functions are constant. Thus:

$\frac{\hbar^2}{2m} \frac{1}{X(x)} \frac{d^2 X}{dx^2} = E_x$, $\frac{\hbar^2}{2m} \frac{1}{Y(y)} \frac{d^2 Y}{dy^2} = E_y$ and $\frac{\hbar^2}{2m} \frac{1}{Z(z)} \frac{d^2 Z}{dz^2} = E_z$ (with $E = E_x + E_y + E_z$).

Consequently, we obtain three independent SSE. The total energy E is the sum of the corresponding eigenenergies E_x, E_y and E_z.

(3) <u>central potential</u>

The separation of variables for the case of a central potential is shown in 5.2.

- *When you use separation of variables in the TDSE, does the $f(t)$ just go away?*

  As seen above, $f(t)$ is the solution of $i\hbar \frac{\partial}{\partial t} f(t) = E f(t)$. It is thus proportional to $e^{-iEt/\hbar}$. $f(t)$ is important to relate $\psi(\overrightarrow{r})$ (solution of the SSE) to $\Psi(\overrightarrow{r}, t)$ (solution of the TDSE): $\Psi(\overrightarrow{r}, t) = f(t)\psi(\overrightarrow{r}) = A e^{-iEt/\hbar} \psi(\overrightarrow{r})$ (A constant).

3 Operators, Expectation Values

3.1 Dealing with Operators

- *How many specific oprerators do we need to know?*

  You need to know the position operator $\hat{\overrightarrow{r}} = \overrightarrow{r}$, the momentum operator $\hat{\overrightarrow{p}} = -i\hbar \overrightarrow{\nabla}$, and all the operators which are constructed from them (kinetic energy operator, potential energy operator, Hamiltonian, angular momentum operator, square of the angular momentum operator...). You also need to become very comfortable with the correspondence principle.

- *How does the potential relate to the energy?*

  The total energy is the sum of two parts (kinetic + potential). The operator associated with the total energy is the Hamiltonian $\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\overrightarrow{r})$. The operator associated with the potential energy is $\widehat{V(\overrightarrow{r})} = V(\overrightarrow{r})$. In one of the problem set, we have seen that the potential energy for an electron in an hydrogen atom is twice the total energy, but this is a very particular case.

3.2 Hamiltonian, Total Energy

- *For the hydrogen atom, we wrote that the Hamiltonian is equal to 3 different things. How come?*

  We indeed wrote:

  $\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$

$$\hat{H} = -\frac{\hbar^2}{2m}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}\right\} - \frac{e^2}{4\pi\epsilon_0 r}$$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{\hat{L}^2}{2mr^2} + V(r).$$

The three expressions are the same because (refer to Lecture 5).

3.3 Angular Momentum

- *What exactly are $\hat{L}_z$, $\hat{L}^2$ and $\hat{H}$ for?*

  How are they used in problems?

  What is the application of $\hat{L}_z$, $\hat{L}^2$ and $\hat{H}$, and their meaning?

  $\hat{L}_z$, $\hat{L}^2$ and $\hat{H}$ are symbols which represent long expressions which include a lot of derivatives (they are called differential operators). In spherical coordinates,

  $$\hat{H} = -\frac{\hbar^2}{2m}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}\right\} + V(r,\theta,\phi)$$

  $$\hat{L}^2 = \frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta} - \frac{1}{\hbar^2\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}$$

  $$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

  Using these operators long equations can be rewritten conveniently (e.g. the SSE can be written in the compact form $\hat{H}\psi = E\psi$)

  $\hat{L}_z$ is the operator associated to the projection of the angular momentum on the z-axis. $\hat{L}^2$ is the operator associated with the square modulus of the angular momentum. The angular momentum is important for problem with spherical symmetry. $\hat{L}_z$, $\hat{L}^2$ are useful to solve SSE's in which the potential is central (that is, spherically-symmetric: V does not depend on θ or ϕ). Indeed, when V is central, $\hat{L}_z$, $\hat{L}^2$ commute with the Hamiltonian $\hat{H}$ (cf. next part)

3.4 Commutation

- *Why is it significant that $\hat{L}_z$, $\hat{L}^2$ and $\hat{H}$ commute?*

  What does it mean if operators have a common set of eigenvalues?

  I still do not understand what a set of commuting operators is.

  The fundamental property of commuting operators is the following:

  "Commuting Hermitian operators have a common set of EIGENFUNCTIONS" (Lecture 5)

  (the corresponding eigenvalues are in general not the same)

  This property is useful to solve difficult eigenvalue problems.

  In the particular case of the Hydrogen atom:

i) It can be verified that $\hat{L}^2$, L_z and $\hat{H}$ commute between one another [2].

ii) Simultaneous eigenvalues of $\hat{L}^2$ and $\hat{L}_z$ have the general form $R(r)Y_{lm}(\theta, \phi)$ (where $R(r)$ can be any function and $Y_{lm}(\theta, \phi)$ are spherical harmonics).

From the preceding, it was inferred in Lecture 5 that the eigenfunctions of $\hat{H}$ have the general form $\psi(r, \theta, \phi) = R(r)Y_{lm}(\theta, \phi)$.

4   Normality, Orthogonality

- *Why do we normalize wavefunctions?*

  As seen above (1.1), the wavefunction can be use to calculate the probability of finding the particle in a spatial region. The meaning of the normality condition: $\int_{space} \psi^*(\overrightarrow{r})\psi(\overrightarrow{r})d\overrightarrow{r} = 1$ is that the sum of all the probabilities must be equal to one (refer to recitation 1 problem III (a)).

- *Why would a wavefunction not be normalized?*

  If two wavefunctions ψ_a and ψ_b are eigenfunctions of the same Hermitian operators, there are always orthogonal (that is, $\int_{space} \psi_a^*(\overrightarrow{r})\psi_b(\overrightarrow{r})d\overrightarrow{r} = 0$). But, unless otherwise specified, nothing guarantees that the wavefunctions are normalized ($\int_{space} \psi_a^*(\overrightarrow{r})\psi_a(\overrightarrow{r})d\overrightarrow{r}$ and $\int_{space} \psi_b^*(\overrightarrow{r})\psi_b(\overrightarrow{r})d\overrightarrow{r}$ are in general different from 1).

5   Hydrogen Atom, Orbitals

5.1   Spherical Harmonics, Radial Functions

- *I am still not great about spherical harmonics*

  I don't understand what Y_{lm} and R_{nl} are.

  How do we obtain quantum numbers from $\hat{L}_z$ and $\hat{L}^2$?

  Spherical Harmonics come from solving simultaneously the eigenvalue equations

  $\hat{L}^2\psi = \text{constant} \times \psi$ and $\hat{L}_z\psi = \text{another constant} \times \psi$

  (this is possible because $[\hat{L}^2, \hat{L}_z] = 0$ commute).

  The general solutions of this double eigenvalue problem is $R(r)Y_{lm}(\theta, \phi)$. Since $\hat{H}$ also commute with L_z and $\hat{L}^2$ (provided that we deal with a central potential), the eigenfunctions of $\hat{H}$ (that is, the soltutions of the SSE) have the same form.

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[2]To show that the commutators $[\hat{H}, \hat{L}^2]$, $[\hat{H}, L_z]$ and $[\hat{L}^2, L_z]$ are zero, the following relations may be useful: $\hat{H} = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{\hat{L}^2}{2mr^2} + V(r)$, $\hat{L}^2 = \frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta} - \frac{1}{\hbar^2\sin^2(\theta)}\hat{L}_z^2$ (which mean that all the θ, ϕ-dependence of $\hat{H}$ is in $\hat{L}^2$, and all the ϕ-dependence of $\hat{L}^2$ is in $\hat{L}_z$).

Making this *ansatz* in the SSE, we obtain an eigenvalue equation for $R(r)$.

This equation is then solved to determine $R(r)$ and the corresponding eigenenergies (Lecture 5 and Engel, Reid: 20.2 - note that $Y(\theta, \phi) \equiv \Theta(\theta)\Phi(\phi)$).

- *What is the significance of spherical harmonics? How do we calculate them?*

  Where do the $\hat{L}^2 Y_{lm} = \hbar^2 l(l+1) Y_{lm}$ and $\hat{L}_z Y_{lm} = m\hbar Y_{lm}$ come from?

  How does the $l(l+1)$ arise?

  In high school, the exponentials $\exp(\alpha x)$ is often introduced as the solution of the differential equation $df(x)/dx = \alpha f(x)$ (note that this is an eigenvalue problem). Similarly, the spherical harmonics $Y_{lm}(\theta, \phi)$ can be introduced as the simultaneous solutions of the eigenvalue problems $\hat{L}^2 Y = \text{constant} \times Y$ and $\hat{L}_z Y = \text{another constant} \times Y$. This eigenvalue problem can be solved by making the *ansatz*: $Y(\theta, \phi) = P(cos(\theta))\Phi(\phi)$ (where P is an unknown polynomial and α is an unknown function) [3].

5.2 Separation of Variables

- Separation of variables for the hydrogen atom?

  Since the potential is central ($V = V(r) = -e^2/(4\pi\epsilon_0 r)$), one can try to separate variables in the SSE: $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$.

  The commutation between $\hat{H}$, $\hat{L}^2$ and $\hat{L}_z$ tell us that $\psi(r, \theta, \phi) = R(r)Y_{lm}(\theta, \phi)$, where $Y_{lm}(\theta, \phi)$ is a spherical harmonic.

  Substituting in the SSE $\hat{H}\psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$ (recall that $\hat{H} = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{\hat{L}^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r}$) we obtain the equation $-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2 R(r) + \frac{\hbar^2 l(l+1)}{2mr^2}R(r) - \frac{e^2}{4\pi\epsilon_0 r}R(r) = ER(r)$ (the first term corresponds to the radial kinetic energy, the second to the angular kinetic energy/centripetal contribution to the energy, and the third to the potential/Coulomb energy). This equation can be solved by making another *ansatz*: $R(r) = L(r)e^{\alpha r}$ (where $L(r)$ and unknown polynomial and α an unknown constant). Refer to Engel, Reid: 20.3.

5.3 Orbitals

- *What exactly does the orbital drawing mean? Do the 3D pictures indicate the probability of the electron being at a certain angle θ, ϕ? What do they say about the distance from the nucleus?*

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[3]The origin of the $l(l+1)$ is more mysterious. In differential analysis, spherical harmonics are introduced as the solutions of $\nabla^2 r^l Y(\theta, \phi) = 0$ (this definition is perhaps more "natural"). You can check for yourself that this is strictly equivalent to $\hat{L}^2 Y = \hbar^2 l(l+1)Y$. This may help to rationalize the $l(l+1)$.

Yes, the spherical harmonic drawings (Engel, Reid Figure 18.7) indicate the probability of the electron being at a certain angle θ, ϕ.

These graphs do not say anything for the electron distance from the nucleus. This distance is related to the radial functions (Engel, Reid Figure 20.6).

To collect information about the angular probability and the radial probability, one can draw a contour plot of the orbitals (Engel, Reid Figure 20.7)

6   Dirac Notations, Integration

- *What is the Dirac notation?*

  You need to know:

  $\hat{A}|\psi\rangle \equiv \hat{A}\psi$

  $\langle\psi|\hat{A} \equiv \hat{A}\psi^*$

  $\langle\psi_a|\hat{A}|\psi_b\rangle \equiv \int_{space} \psi_a^*(\overrightarrow{r})\{\hat{A}\psi_b(\overrightarrow{r})\}d\overrightarrow{r} = \int_{space}\{\hat{A}\psi_a(\overrightarrow{r})\}^*\psi_b(\overrightarrow{r})d\overrightarrow{r}$ ($\hat{A}$ is supposed to be Hermitian)

- *I am still having problem with integrating a particle in a box.*

  For a particle in an infinite box, since the particle is confined within the box, the integrations must be done over the spatial region $0 < x < a$, $0 < y < b$ and $0 < z < c$ (a, b and c are the dimensions of the box).

  For the finite box, you need to integrate over all space because the particle can go outside the box (quantum tunnelling, exponential tail).