PHY294 Quantum and Thermal Physics

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Syllabus

Section	Time	Session 1	Session 2	Session 3	Session 4
PRA 0104 AM1	9am-12pm	January 10	January 31	February 28	March 20
PRA 0101 PM1	2pm-5pm				
PRA 0105 AM2	9am-12pm	January 17	February 7	March 6	March 27
PRA 0102 PM2	2pm-5pm				
PRA 0106 AM3	9am-12pm	January 24	February 14	March 13	April 4
PRA 0103 PM3	2pm-5pm				

Assessment	Weight (%)	Dates
Tutorial Quizzes	10%	4 quizzes
Midterms*	30% (15% + 15%)	Tuesday, Feb. 6, 2024 (Part 1) Thursday, Mar. 28, 2024 (Part 2)
Lab Reports (4 lab weights)	20%	2nd Friday after completing the lab
Final Exam	40%	Scheduled by the Office of the Faculty Registrar in the Final Exam Period

*Midterm 1 will be based on material from lectures 1 - 11 of Part 1 and Midterm 2 will be based on material from lectures 1 - 13 of Part 2. If one midterm is missed due to an excused absence the weight will be transferred to the corresponding half of the final exam.

TZD 7.4: The Particle in Rigid Box

- Infinite Square Well. The wave function is 0 outside the domain of the box. $\psi(x) = 0 \forall]0, a[$

- Guess $\psi(x) = A\sin(kx) + B\cos(kx)$

- Boundary conditions: $\psi(0) = \psi(a) = 0 \implies A\sin(ka) = 0 \implies ka = n\pi$

- $k = \frac{n\pi}{a} \implies \lambda = \frac{2a}{n} \implies p = \frac{n\pi\hbar}{a} \implies E_n = n^2\frac{\pi^2\hbar^2}{2ma^2}$

> **Important:**
>
> The energy of a particle in an 1D ISW of width a is quantized
>
> $$E_n = n^2 \frac{\pi^2 \hbar^2}{2ma^2}$$

TZD 7.5: Time-Independent Schrödinger Equation

- It is natural to assume that the behaviour of a quantum system to be similar to a classical wave. The wave equation.

- Start off with $\psi(x) = A\sin(kx)$

- Differentiate twice to give $\frac{d^2\psi}{dx^2} = -Ak^2\sin(kx)$

- By observation, we see that the first derivative is proprtional to the second: $\frac{d^2\psi}{dx^2} = -k^2\psi \implies \frac{d^2\psi}{dx^2} = -\frac{2mK}{\hbar^2}\psi$

- Note that we replace Kinetic energy with Total minus Potential (useful for ISW): $K = E - U(x)$

> **Important:**
>
> The TISE is given as the following second order differential equation:
>
> $$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}[U(x) - E]\psi$$

TZD 7.6: The Rigid Box Again

- Rederive the energy states of a 1D ISW using the TISE

- ...

- We end up with $\psi(x) = A\sin(\frac{n\pi x}{a})$.
    - This function satisfies the TISE and the boundary conditions, so what can constrain A?

- Recall, $|\psi(x)|^2$ is the probability density for finding the particle at x

- **For a 1 dimensional system,** this means finding the particle between $x + dx$

- Thus, since the total probability of finding the particle anywhere is 1 (the normalization condition)

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1$$

- In this case $A = \sqrt{\frac{2}{a}}$

> **Important:**
>
> Normalization:
>
> $$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1$$
>
> ISW:
>
> $$\psi(x) = \sqrt{\frac{2}{a}}\sin(\frac{n\pi x}{a})$$

TZD 8.2: The Three-Dimensional Schrödinger Equation

- $\psi = \psi(x, y, z) = \psi(\mathbf{r})$

- $U = U(x, y, z) = U(\mathbf{r})$

- Note that E does not necessarily depend on $\mathbf{r}$ and can take on various values

-
$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} = \frac{2M}{\hbar^2}[U(\mathbf{r}) - E]\psi$$

TZD 8.3: The Two-Dimensional Square Box

- Same thing as the 1D case but extended to the x, y plane

-
$$f(x, y) = \begin{cases} 0 & \text{if } 0 \le x \le a \text{ and } 0 \le y \le a, \\ \infty & \text{else} \end{cases}$$

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} = \frac{2M}{\hbar^2}[U - E]\psi$$

- We assume that the wave function is separable i.e. $\psi(x, y) = X(x)Y(y)$, as this allows us to simplify the PDE into two ODEs

- By differentiating, we get $X''(x)/X(x) = \text{constant} = -k_x^2$ and $Y''(y)/Y(y) = \text{constant} = -k_y^2$

- This is the same form as the 1D case, as the sine function satisfies

-
$$\psi(x, y) = A \sin \frac{n_x \pi x}{a} \frac{n_y \pi y}{a}$$

- In order to find the allowed energies we plug the expressions, back into
$$\frac{X''}{X} + \frac{Y''}{Y} = -\frac{2ME}{\hbar^2}$$

- Recall the sine terms cancel out, and we are left with constants k_x and k_y which can be expressed as **quantum numbers** (integers) n_x and n_y

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Important:

The allowed Energies for a 2D box of length a

$$E = E_{n_x, n_y} = \frac{\hbar^2 \pi^2}{2Ma^2}(n_x^2 + n_y^2)$$

- **Degeneracy:**
  - If two or more combinations of n_x and n_y give rise to the same energy level, E_{n_x, n_y}, then the energy level is called degenerate.
  - $E_{55} = E_{17} = E_{71}$ are all degenerate
  - E_{11} is non degenerate

TZD 8.5: The Three-Dimensional Central-Force Problem

- Now, let us work within our hydrogen atom in order to model the wave function of its electron:

-
$$\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] + = \frac{2M}{\hbar^2}[U(\mathbf{r} - E]\psi$$

- Separation of variables leads to $\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$

- The same procedure occurs, and we get that $\Phi''/\Phi = f(r, \theta) = -m^2$

- Then $g(\theta) = h(r) = -k$, since both sides of the equation are separated, then the other side must be a constant, so we can also solve for Θ and R . Thus we hvae $\psi(r, \theta, \phi)$

Important:

Φ equation:
$$\Phi''(\phi) = -m^2\Phi(\phi)$$

Θ equation:
$$\frac{1}{\sin(\theta)}\frac{d}{d\theta}(\sin(\theta)\frac{d\Theta}{d\theta}) + (k - \frac{m^2}{\sin^2(\theta)})\Theta = 0$$

R equation:
$$\frac{d^2}{dr^2}(rR) = \frac{2M}{\hbar^2}[U(r) + \frac{k\hbar^2}{2Mr^2} - E](rR)$$

TZD 8.6: Quantization of Angular Momentum

The Φ equation

- Recall the Φ ODE is given as $\Phi''/\Phi = f(r, \theta) = -m^2$

- $\Phi(\phi) = e^{im\phi}$ must be periodic, so $m = Z$

- The significance of m is the same as in two dimensions: by fixing r and θ by letting ϕ vary, we move around a circle about the z axis. The radius of the circle is $\rho = r\sin(\theta)$

- Through some manipulations (irrelevant), we get that the z component of the ancular momentum is $L_z = m\hbar$, for $m = Z$

    - Note, this was exactly Bohr's assumption (except he didn't account for total momentum **L**

The Θ equation

- The Θ equation is the Legendre's Equation which will not be solved here

- In any case, the equation has one solution for k which is again quantized $k = l(l + 1)$, where l is a positive integer greater than or equal in magnitude to m $l \geq |m|$

- Thus, we may denote the acceptable solutions by $\Theta_{lm}(\theta)$

- Our solution has the form

Quantum Addresses

- Magnitude of the angular momentum $||\mathbf{L}|| = \sqrt{l(l + 1)}\hbar$

- $l = 0, 1, 2, ...$

- $L_z = m\hbar$

- $m = l, l - 1, ...0, ..., -l$. Any integer less than or equal in magnitude to l

TZD 8.7: The Energy Levels of the Hydrogen Atom

- Recall that separation of variables lead to the following equation for R. Note $k = l(l+1)$

- Recall that the Coulomb potential (derived from the Coulomb force) for the electron is $U(r) = -\frac{ke^2}{r}$

$$\frac{d^2}{dr^2}(rR) = \frac{2m_e}{\hbar^2}[-\frac{ke^2}{r} + \frac{l(l+1)\hbar^2}{2m_e r^2} - E](rR)$$

- $E = -\frac{m_e(ke^2)^2}{2\hbar^2}\frac{1}{n^2}$

> **Important:**
>
> - $n = 1, 2, 3...$
> - $l = 0, 1, 2, ..., (n-1)$
> - $m = l, l-1, ..., -l$
> - $(m_s = \pm 1/2)$ (for electrons)

TZD 8.8: Hydrogenic Wave Functions

- Ground state: $n = 01, l = 0 \implies m = 0$

- Since $l = 0, m = 0$ the wave function must be radially symmetric

$$\psi_{1s}(r, \theta, \phi) = R_{1s}(r)$$

- By plugging $l = 0$ into the radial ODE, we get the following radial function Ae^{-r/a_B}, where a_B is the Bohr radius

- Note we are now working in spherical coordinates, so the radial probability density is $P(r) = 4\pi r^2|R(r)|^2$

- The probability density function of the 1s state is $P_{1s} = r\pi A^2 r^2 r^{-2r/a_B}$

- Note that there is a maximum at exactly a_B

> **Important:**
>
> Find any wave function by plugging in the quantum address n, l, m into the three ODEs. Note this only works for $m_s = \pm 1/2$ and for the 1 body problem.
>
> $$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)\Theta_{lm}(\theta)e^{im\phi}$$

TZD 8.9: Shells $n > 1$ + Multiple electrons

TZD 8.10: Hydrogen-Like Ions

- Consider ions with $Z > 1$ and 1 electron

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$$E = -\frac{m(ke^2)^2}{2\hbar^2}\frac{1}{n^2} = -Z^2\frac{E_R}{n^2}$$

- **Replace** a_B with a_B/Z

TZD 9.2: Spin Angular Momentum

- Total angular momentum $\mathbf{J}$ equals to the orbital and spin angular momentum: $\mathbf{J} = \mathbf{L} + \mathbf{S} \to \mathbf{r} \times \mathbf{p} + I\omega$

- Recall that the mangitude of the the orbital angular momentum is quantized and is equal to $||\mathbf{L}|| = \sqrt{l(l+1)}\hbar$

  - $L_z = m\hbar$
  - $m = l, l-1, ..., -l$

- Similarly, $||\mathbf{S}|| = \sqrt{s(s+1)}\hbar$

  - $S_z = m_s\hbar$
  - Where $m_s = \pm\frac{1}{2}$

- However, note that for an electron, $s = \frac{1}{2}$ always

- Thus, the electron's spin angular momentum is always $||\mathbf{S}|| = \frac{\sqrt{3}}{2}\hbar$

> **Important:**
>
> Note, l, m, m_s has no effect on the energy of the electron. The degerenacy of the nth level in hydrogen is $2n^2$

TZD 9.3: Magnetic Moments

- Consider a loop of area A of current i flowing within a magnetic field $\mathbf{B}$. The torque experienced by the loop is equal to $\mathbf{\Gamma} = i\mathbf{A} \times \mathbf{B}$

  - Note that $\mathbf{A}$ is a vector with magnitude as the area of the loop and direction, normal to the plane.
  - $U = -\boldsymbol{\mu} \cdot \mathbf{B}$
  - $\mu = i\mathbf{A} = -\frac{e}{2m_e}\mathbf{L}$, the mangetic moment

TZD 9.4: The Zeeman Effect

- The motion of electrons is inherently a current and thus has a magnetic moment $\boldsymbol{\mu}$

- Thus, in the presence of a magnetic field $\mathbf{B}$, we can change the atom's energy levels by a quantized amount $-\boldsymbol{\mu} \cdot \mathbf{B}$

- From algebraic maniuplation: $\Delta E = m\mu_B B$

TZD 9.5: Spin Magnetic Moments

- Orbital spin: $\boldsymbol{\mu_{orb}} = -\frac{e}{2m_e}\mathbf{L}$
- Spin gyromagnetic ratio: $\boldsymbol{\mu_{spin}} = -\frac{e}{m_e}\mathbf{S}$

TZD 9.6: The Anomalous Zeeman Effect

- "Mulitplets" of lines: when an atom is placed in a magnetic field. Small shifts in spectral lines.

TZD 10.2: Independent-Particle Approximation

- The Schrödinger equation dor one eletron moving around a nucleus of charge Z can be solved analytically

- With 2 or more electrons the starting point for all calculations is called the **independent-particle approximations**, (IPA)

    - Essentially considering the forces between the electrons independently, then corrrecting later for the attraction forces between the electrons.
    - Assume that the $Z - 1$ other electrons are distributed spherically symetric around the nucleus. Thus, $U(\mathbf{r}) = U(r)$

- For an electron close enough to the nucleus, it experiences the full charge $F = \frac{ke^2}{r^2}$

- For an electron outside all its fellow electrons experiences a force of the nucleus Ze minus (Z-1)e. Thus, the force is the same as that experienced by an electron in the hydrogen atom:

$$F = \frac{ke^2}{r^2} \implies U(r) = -\frac{ke^2}{r}$$

    - Where r is touside all the other electrons.
    - If $r \to 0$, $U(r) \approx -\frac{Zke^2}{r}$

Important:

The potential energy $U(r)$ experienced by the electron in question is given by

$$U(r) = -Z_{eff}(r)\frac{ke^2}{r}$$

Where $Z_{eff}(r)$ isa function of the radius and is the **effective charge** "felt" by the electron.
  1. When r is inside the other electrons $Z_{eff} \to Z$ (the atomic number of the atom)

  2. When r increases, the nuclear charge is shielded or screened by more and more of the electrons, $Z_{eff} \to 1$

TZD 10.3: The IPA Energy Levels

- The 1s wave function approximates to that of a hydrogen-like ion with nuclear charge Ze; the 1s energy is close to $-Z^2 E_R$

- The next energy level is $n = 2$, however, this is different as the **2s and 2p states are degenerate in hydrogen.** Whereas in multieletcron atoms, the 2s states are lower in energy.

- The 2p and 2s probability density functions are concentrated further than 1 a_B, thus, the electron density is screened and shielded by the 1s electron; however, the 2s function has a smaller local maximum at around $0.7a_B$, thus experiences, on average minimal screening, meaning that $Z_{eff} \approx Z$. This means that a 2s electron is more strongly attracted to the nucleus than a 2p electron.

TZD 10.4: The Pauli Exclusion Principle

- Consider the possible states of the whole atom s.t the energy of the atom is minimized

- **No two electrons ins quantum system can occupt the same quantum state**

- Example consider Helium $Z = 2$, if we add one electron to the nucleus, its lowest possible states is the 1s state $(n = 1, l = m = 0)$.

- **Ground State:** The degeneracy of helium 1s is $2(1)^2 = 2$, thus two electrons must occupy different spin states: $m_s = \pm\frac{1}{2}$, as the quantum states must be different. **The spin cancels** and there is

- **Excited State:** Consider the lowest excited state of helium with an electron in state $1, 0, 0, 1/2$ and an electron in state $2, 0, 0, 1/2$.

  - The second electron occupies the 2s or 2p orbital; however, the 2p wave function is on average further from the nucelus and thus experiences more shielding from the 1s electron. Thus, 2s is more favourable in terms of energy.
  - The electrons can be anti or parallel.

TZD 12.1: Molecules - Introduction

- Molecule is a stable/near stable bound state of two or more atoms. This state is bound via a shared pair of electrons

TZD 12.4: The Covalent Bond

- Consider the H_2^+ molecular ion:

- The protons are heavy relative to the electorn so assume that they are stationnary.

- Then we solve the Schrödinger equation for the one electron to find its lowest allowed energy E. This energy will depend on the internuclear distance R that is find the R_0 such that $\frac{dE}{dR} = 0$

- **Assume that the distance between the two protons are larger than the bohr analysis.**

- The solutions of the equation are easy to see. If the electron is close to proton 1, the effect of the distant proton 2 is small and the lowest possible state is the ground state for **the hydrogen ground state**. The corresponding wave function for the first proton is $\psi_1(\mathbf{r}) = Ae^{-r_1/a_B}$ The second state is the same thing for proton 2 $\psi_2(\mathbf{r}) = Ae^{-r_2/a_B}$

- Note that the solution is a linear combination

$$\psi = B\psi_1 + C\psi_2$$

- $\psi_+ = \psi_1 + \psi_2$ Occurs when the wave functions interfere constructively. THis leadas to an enhanced electron density between the two protons. **Bonding**

- $\psi_- = \psi_1 - \psi_2$ Occurs when the wave functions interfere **destructively**. This leads to a reduced density. **Anti-Bonding**

- Note that $|\psi(x)|^2 = |\psi(-x)|^2$, with either $\psi = \psi_+ = \psi_-$, meaning that the electron distirbution at any point near proton 1 is the same as that near proton 2.

-

- The ψ_+ and ψ_- are the molecular orbitals since they describe states that associated with both protons.

Bonding

- sigma bond is the head on overlapping of atomic orbitals.

- pi bond is the lateral overlap of p orbitals.

- N_2 has one sigma bond and two pi bonds

As an example consider water:

- Valence electron configuration of O: $2s^2 \ 2p_x^2 \ 2p_y^1 \ 2p_z^1$

- Valence electron configuration of H: $1s^1$

- The two unpaired p orbitals of hydrogen form a sigma bond with the hydrogen

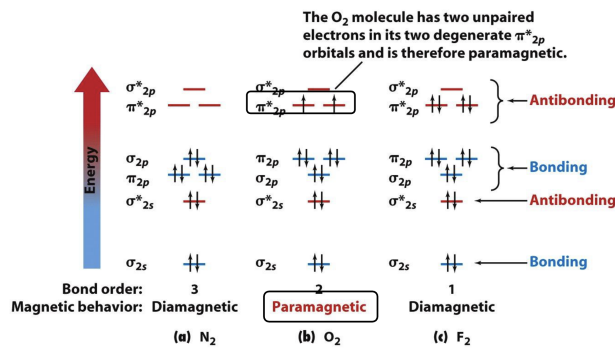**The O₂ molecule has two unpaired electrons in its two degenerate π*₂ₚ orbitals and is therefore paramagnetic.**

Figure 1: Enter Caption

Lecture Important Notes 9 Monday January 29

- Electron distribution for bonding -¿ perturbation/change in electron density from original hydrogenic central force problem.

- Fourier Theorem: reconstructing arbitrary functions from a sum of sine waves with carying frequencies

    - Adding more functions gets closer to the truth

- Lower in energy: bonding $\psi_1 + \psi_2$

- Higher in energy: anti-bonding $\psi_1 - \psi_2$

- Orbital Overlaps:

    - Anti-bonding: linear combination creates decrease in electron density

- Molecular orbital theory:

    - H2: 1s orbital of hydrogen A, 1s orbital of hydrogen 2s
    - Energy is lower for bonding pair
    - Energy is **symmetrically** higher for anti-bonding pair
    - He: will not form a bond because electrons take up bonding and anti-bonding position: cancels out
    - Bond order = number of bonding electrons - number of anti bonding electrons
    - HOMO: highest occupied molecular orbital
    - LUMO: lowest unoccupied molecular orbital
    - $O_2 : Z = 8 > 7$ so
        * Orbital Mixing:
            · $Z > 7, \sigma_p < \pi$
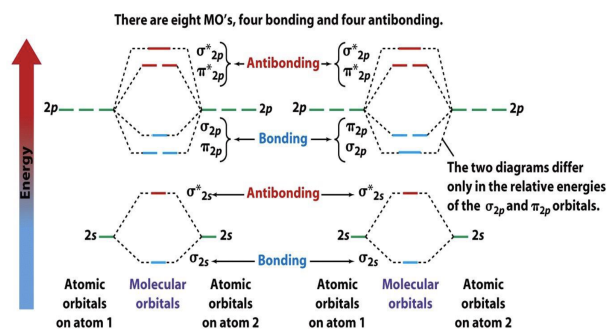   · $Z \leq 7, \pi < \sigma_p$

Figure 2: Enter Caption