

Honors Physical Chemistry I
Chem 3890
 Review outline for Final Exam

LAST REVISED: November 23, 2011

The Final Exam is on Thursday, December 8, 2:00 - 4:30 pm,
 Rockefeller Hall 201 (Schwartz Aud).
The exam will cover all the course material. Therefore, *in addition* to the topics listed below, you will need to study the material on the two Prelim review sheets.
 You may use a calculator. Devices that store text or that have infrared transmitters are *not* permitted.

1. Hydrogen atom

[McQ&S, Chapter 6; Griffith, 4.2]

Set $Z = 1$, $\mu \rightarrow m_e$ (mass of electron)

Radial Schrödinger equation for radial wavefunction $\mathcal{R}(r)$

$$-\frac{\hbar^2}{2\mu} \left[\mathcal{R}'' + \frac{2}{r} \mathcal{R}' \right] + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} \mathcal{R} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \mathcal{R} = E \mathcal{R}$$

Effective potential $V_{\text{eff}}(r) = V(r) + \frac{\hbar^2 \ell(\ell+1)}{2mr^2}$

Limiting form of radial wavefunction $u \equiv r\mathcal{R}(r)$:

$u(r) \sim r^{\ell+1}$ as $r \rightarrow 0$ (regular solution)

$u(r) \sim e^{-\kappa r}$ as $r \rightarrow \infty$, $\kappa \equiv \sqrt{-2\mu E}/\hbar$

$\Rightarrow u(r) \sim r^{\ell+1} \times e^{-\kappa r} \times$ (Polynomial in r)

Unit of length $a_0 \equiv (4\pi\epsilon_0/e^2) \times (\hbar^2/m_e)$ (Bohr radius)

Unit of energy $\mathbb{R} \equiv (e^2/4\pi\epsilon_0) \times 1/(2a_0)$ (Rydberg)

Quantized energies $E_n = -\mathbb{R}/n^2$, $n = 1, 2, \dots$

Radial QN n : $\mathcal{R}_{n\ell}(r)$, $u_{n\ell}(r)$

Radial wavefunctions (no need to memorize details of the Laguerre polynomials or of normalization factors, etc; you do need to know the structure $\mathcal{R} \sim r^\ell \times \text{polynomial} \times \text{exponential}$).

$$\mathcal{R}_{n\ell}(r) = \sqrt{\frac{(n-\ell-1)!}{2n(n+\ell)!}} \left(\frac{2}{na_0} \right)^{\ell+\frac{3}{2}} r^\ell e^{-r/na_0} L_{n-\ell-1}^{2\ell+1} \left[\frac{2r}{na_0} \right] \begin{cases} n = 1, 2, \dots \\ \ell = 0, 1, \dots, n-1 \end{cases}$$

Associated Laguerre polynomial $L_{n-\ell-1}^{2\ell+1}[2r/na_0]$ (Mathematica conventions)

$(n-\ell-1)$ = number of radial nodes for $0 < r < \infty$

Total number of nodal surfaces in wavefunction $\psi_{n\ell m}(r, \theta, \phi)$: $|m| + (\ell - |m|) + (n - \ell - 1) = n - 1$

Radial probability density: $\mathcal{P}_{n,\ell}(r) = r^2 |\mathcal{R}_{n,\ell}(r)|^2 = |u_{n,\ell}(r)|^2$

$\int_0^\infty dr \mathcal{P}_{n,\ell}(r) = 1$.

2. Angular momentum & magnetic fields

[McQ&S, prob 6.43 - 6.47; Griffith, 4.3]

Analogy: electric dipole \mathbf{d} in E-field \mathbf{E} : interaction energy $H' = -\mathbf{d} \cdot \mathbf{E}$

Current loop \Rightarrow magnetic moment $\mathbf{M} = \frac{q}{2m} \mathbf{L}$

Magnetic moment in B-field, interaction energy $H' = -\mathbf{M} \cdot \mathbf{B}$

Electron, charge $q = -e$, mass $m = m_e$, \mathbf{B} along z -axis:

$$H' = \beta B m, \beta \equiv e\hbar/2m_e, \text{ Bohr magneton}$$

$$E_{n,m} = E_n + \beta B m$$

Inhomogeneous B -field: $\mathbf{B} = \mathbf{B}(\mathbf{R})$, $H' = -\mathbf{M} \cdot \mathbf{B}(\mathbf{R})$ (\mathbf{R} = position of atom center of mass)

Variation of H' with $\mathbf{R} \Rightarrow$ force on atom CM, direction depending on n .

Stern-Gerlach experiment: $B_z = B_z(z)$, AM $L \Rightarrow (2L + 1)$ distinct spots at screen

3. Spin: intrinsic AM

Griffith, 4.4

Beam of Ag atoms ($L = 0$) \Rightarrow 2 spots \Rightarrow spin AM $s = \frac{1}{2}$ $m_s = \pm \frac{1}{2}$

Operators: \hat{S}^2, \hat{S}_z . QN: s, m_s . Eigenstates $|s, m_s\rangle$

Spin- $\frac{1}{2}$: spin states $\{|\frac{1}{2}, +\frac{1}{2}\rangle, |\frac{1}{2}, -\frac{1}{2}\rangle\}$

$$\hat{S}^2 |\frac{1}{2}, m_s\rangle = \hbar^2 \frac{1}{2} (\frac{1}{2} + 1) |\frac{1}{2}, m_s\rangle = \hbar^2 \frac{3}{4} |\frac{1}{2}, m_s\rangle$$

$$\hat{S}_z |\frac{1}{2}, m_s\rangle = \hbar m_s |\frac{1}{2}, m_s\rangle, m_s = \pm \frac{1}{2}.$$

General spin- $\frac{1}{2}$ state $|\chi\rangle = |\frac{1}{2}, +\frac{1}{2}\rangle c_+ + |\frac{1}{2}, -\frac{1}{2}\rangle c_-$, with $c_{\pm} = \langle \frac{1}{2}, \pm \frac{1}{2} | \chi \rangle$

Measure $\hat{S}_z \rightarrow m_s = +\frac{1}{2}\hbar$, prob $|c_+|^2$, $m_s = -\frac{1}{2}\hbar$, prob $|c_-|^2$

4. Identical \equiv indistinguishable particles in QM

Griffith, 5.1.

Observable quantities cannot depend on the labelling of identical particles, and are invariant under permutations of labels of identical particles.

$$\Rightarrow \mathcal{P}_{12}\Psi(1, 2) \equiv \Psi(2, 1) = \pm\Psi(1, 2)$$

Identical FERMIONS: $\mathcal{P}_{12}\Psi(1, 2) = -\Psi(1, 2)$

Identical BOSONS: $\mathcal{P}_{12}\Psi(1, 2) = +\Psi(1, 2)$

Spin-statistics relation: FERMIONS have spin $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$ BOSONS have spin $0, 1, 2, \dots$

Consider 2 particles in (orthogonal) spatial states ϕ_a, ϕ_b . 3 cases:

- Distinguishable: $\Psi(x_1, x_2) = \phi_a(x_1)\phi_b(x_2)$
- Identical BOSONS: $\Psi_S(x_1, x_2) = \frac{1}{\sqrt{2}} [\phi_a(x_1)\phi_b(x_2) + \phi_b(x_1)\phi_a(x_2)]$ (Symmetric)
- Identical FERMIONS: $\Psi_A(x_1, x_2) = \frac{1}{\sqrt{2}} [\phi_a(x_1)\phi_b(x_2) - \phi_b(x_1)\phi_a(x_2)]$ (Antisymmetric)

$$\langle \Psi_S | (x_1 - x_2)^2 | \Psi_S \rangle < \langle \Psi | (x_1 - x_2)^2 | \Psi \rangle < \langle \Psi_A | (x_1 - x_2)^2 | \Psi_A \rangle$$

\equiv effective *attraction* (BOSONS), effective *repulsion* (FERMIONS)

2 spin- $\frac{1}{2}$ electrons (identical FERMIONS):

Singlet state $\frac{1}{\sqrt{2}}[\alpha_1\beta_2 - \beta_1\alpha_2]$ (Antisymmetric wrt exchange of labels)

Triplet states: $\{\alpha_1\alpha_2, \frac{1}{\sqrt{2}}[\alpha_1\beta_2 + \beta_1\alpha_2], \beta_1\beta_2\}$ (Symmetric wrt exchange of labels)

Possible 2-electron states:

Symmetric spatial wavefunction \times Antisymmetric spin function (Singlet)

Antisymmetric spatial function \times Symmetric spin functions (Triplet)

$N \times N$ Slater determinant \Rightarrow N -electron antisymmetric wavefunction

Spin-orbitals: $\phi(1) \equiv \phi(\mathbf{r}_1) \times \alpha_1, \bar{\phi}(1) \equiv \phi(\mathbf{r}_1) \times \beta_1$

3×3 example (ϕ_a, ϕ_b, ϕ_c orthonormal):

$$\begin{aligned}\Psi(1, 2, 3) &= \frac{1}{\sqrt{6}} \begin{vmatrix} \phi_a(1) & \phi_b(1) & \phi_c(1) \\ \phi_a(2) & \phi_b(2) & \phi_c(2) \\ \phi_a(3) & \phi_b(3) & \phi_c(3) \end{vmatrix} \\ &= \frac{1}{\sqrt{6}} [\phi_a(1)\phi_b(2)\phi_c(3) - \phi_a(1)\phi_b(3)\phi_c(2) - \phi_b(1)\phi_a(2)\phi_c(3) \\ &\quad + \phi_b(1)\phi_a(3)\phi_c(2) + \phi_c(1)\phi_a(2)\phi_b(3) - \phi_c(1)\phi_a(3)\phi_b(2)]\end{aligned}$$

Determinant:

- (i) changes sign upon exchange of rows \equiv built-in antisymmetry wrt exchange of labels
- (ii) vanishes if any 2 columns are the same \equiv Pauli exclusion principle (no 2 electrons can occupy same spin-orbital)

5. Approximation methods: Perturbation theory

McQ&S, 7-4; Griffith, 6.1.

Decompose Hamiltonian into solvable part \hat{H}_0 and nonseparable perturbation \hat{H}'
 $\hat{H} = \hat{H}_0 + \hat{H}'$

Known solutions: $\hat{H}_0 |\psi_n^0\rangle = E_n^0 |\psi_n^0\rangle$

Family of Hamiltonians $\hat{H}(\lambda) = \hat{H}_0 + \lambda\hat{H}'$ where $0 \leq \lambda \leq 1$

To solve: $\hat{H}(\lambda) |\psi(\lambda)\rangle = E(\lambda) |\psi(\lambda)\rangle$

Perturbation of nondegenerate state $|\psi_n^0\rangle$: expand $E_n(\lambda)$ and $|\psi_n(\lambda)\rangle$ in powers of λ

$$E_n(\lambda) = E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots, |\psi_n(\lambda)\rangle = |\psi_n^0\rangle + \lambda |\psi_n^{(1)}\rangle + \dots$$

Plug into Schrödinger equation, expand \Rightarrow

- $E_n^{(1)} = \langle \psi_n^0 | \hat{H}' | \psi_n^0 \rangle$ (1st-order correction to energy)
- $|\psi_n^{(1)}\rangle = - \sum_{m \neq n} |\psi_m^0\rangle \frac{\langle \psi_m^0 | \hat{H}' | \psi_n^0 \rangle}{E_m^0 - E_n^0}$ (1st-order correction to wavefunction)
- $E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \psi_m^0 | \hat{H}' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}$ (2nd-order correction to energy)

Example: PIB with sloping bottom.

6. Approximation methods: Variational principle

Griffith, 7.1; McQ, 7-1.

Exact GS energy E_0 . For any state ψ , $E_0 \leq \langle H \rangle_\psi$

Wavefunction ψ_α . Minimize $\langle \hat{H} \rangle(\alpha) \equiv \langle \psi_\alpha | \hat{H} | \psi_\alpha \rangle / \langle \psi_\alpha | \psi_\alpha \rangle$ wrt α ,
 $\partial \langle \hat{H} \rangle / \partial \alpha = 0 \Rightarrow$ best estimate of GS energy

Ex: $V(x) = \lambda x^4$

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"I still don't understand quantum theory."