

Chemistry 474B 2006-07

Advanced Quantum Chemistry and Spectroscopy

Instructor: Professor Rob Lipson

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Prerequisites: Chemistry 374a

Internet: <http://instruct.uwo.ca/chemistry/474b/>

Lectures: Tuesdays, Thursdays 11:30 am -12:30 pm in CB115.

Wednesday 10:30 am -11:30 am in CB115

Textbook: None required. All suggested books below will be on short term (3-day) loan in the library

- A popular choice is Atoms and Molecules: An Introduction for Students of Physical Chemistry, M. Karplus and R. N. Porter, W. A. Benjamin, Inc. 1970 (QD461.K33).

Other useful books include:

- Molecular Spectroscopy, I. N. Levine, Wiley Interscience, 1975 (QC454.M6L48)

- Quantum Chemistry 5th Edition, I. N. Levine, Allyn and Bacon, Inc., 2000 (QD462.L47 2000)

- Molecular Quantum Mechanics, P. W. Atkins, Oxford University Press, 1983 (QD462.A84 1983)

Evaluation:

One term test of 2 hour duration. Date to be announced: 35%

Final exam: 50%

Problem Sets (~7 in total) 15 %.

Course Outline: Details, emphasis and ordering of the material may change as the course proceeds. Specific mathematical notation and tools will be introduced as they are needed. Some of the material is an extension of that encountered in Chem. 374a/b. It is worthwhile to review those notes in the early part of the course. Some of this material will be reviewed in class as needed.

Possible topics to be covered include:

Time-independent non-degenerate perturbation theory, matrix algebra, time-independent degenerate perturbation theory, time-dependent perturbation theory, selection rules, angular momentum: the basics, coupled and uncoupled representations, application to spin-orbit coupling in H-atoms, many electron atoms: quantum numbers, terms, Slater determinants, energies including Coulomb and Exchange contributions, Variational theory, Hartree-Fock calculations, the periodic table and periodicity trends, Born-Oppenheimer approximation, molecular orbitals versus the valence bond method, etc.

Legal Notice

Unless you have either the requisites for this course or written special permission from your Dean to enroll in it, you will be removed from this course and it will be deleted from your record. This decision may not be appealed. You will receive no adjustment to your fees in the event that you are dropped from the course for failing to have the necessary prerequisites.

Table 4.1. Revised 2005 by C.G. Wohl (LBNL). Adapted from the Commission on Atomic Weights and Isotopic Abundances, "Atomic Weights of the Elements 1999," Pure and Applied Chemistry 73, 667 (2001), and G. Audi, A.H. Wapstra, and C. Thibault, Nucl. Phys. A729, 337 (2003). The atomic number (top left) is the number of protons in the nucleus. The atomic mass (bottom) is weighted by isotopic abundances in the Earth's surface. Atomic masses are relative to the mass of the carbon-12 isotope, defined to be exactly 12 unified atomic mass units (u). Errors range from 1 to 9 in the last digit quoted. Relative isotopic abundances often vary considerably, both in natural and commercial samples. A number in parentheses is the mass of the longest-lived isotope of that element—no stable isotope exists. However, although Th, Pa, and U have no stable isotopes, they do have characteristic terrestrial compositions, and meaningful weighted masses can be given. For elements 110 and 111, the numbers of nucleons *A* of confirmed isotopes are given.

1 IA		PERIODIC TABLE OF THE ELEMENTS																18 VIIIA	
1 H Hydrogen 1.00794	2 He Helium 4.002602											13 B Boron 10.811	14 C Carbon 12.0107	15 N Nitrogen 14.0067	16 O Oxygen 15.9994	17 F Fluorine 18.9984032	18 Ne Neon 20.1797		
3 Li Lithium 6.941	4 Be Beryllium 9.012182											5 Al Aluminum 26.981538	6 Si Silicon 28.0855	7 P Phosph. 30.973761	8 S Sulfur 32.065	9 Cl Chlorine 35.453	10 Ar Argon 39.948		
11 Na Sodium 22.989770	12 Mg Magnesium 24.3050	3 III B	4 IV B	5 V B	6 VI B	7 VII B	8 VIII	9 VIII	10 VIII	11 IB	12 IIB	13 Al Aluminum 26.981538	14 Si Silicon 28.0855	15 P Phosph. 30.973761	16 S Sulfur 32.065	17 Cl Chlorine 35.453	18 Ar Argon 39.948		
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955910	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938049	26 Fe Iron 55.845	27 Co Cobalt 58.933200	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge German. 72.64	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80		
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybd. 95.94	43 Tc Technet. (97.907216)	44 Ru Ruthen. 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.293		
55 Cs Cesium 132.90545	56 Ba Barium 137.327	57-71 Lanthanides	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.078	79 Au Gold 196.96655	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98038	84 Po Polonium (208.982430)	85 At Astatine (209.987148)	86 Rn Radon (222.017578)		
87 Fr Francium (223.019736)	88 Ra Radium (226.025410)	89-103 Actinides	104 Rf Rutherford. (261.10877)	105 Db Dubnium (262.1141)	106 Sg Seaborg. (263.1221)	107 Bh Bohrium (262.1246)	108 Hs Hassium (277.1498)	109 Mt Meitner. (268.1387)	110 Ds Darmstadt. [269.271]	111 [272]									

Lanthanide series

57 La Lanthan. 138.9055	58 Ce Cerium 140.116	59 Pr Praseodym. 140.90765	60 Nd Neodym. 144.24	61 Pm Prometh. (144.912749)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolin. 157.25	65 Tb Terbium 158.92534	66 Dy Dyspros. 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.259	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
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Actinide series

89 Ac Actinium (227.027752)	90 Th Thorium 232.038055	91 Pa Protactin. 231.035884	92 U Uranium 238.02891	93 Np Neptunium (237.048173)	94 Pu Plutonium (244.064204)	95 Am Americ. (243.061381)	96 Cm Curium (247.070354)	97 Bk Berkelium (247.070307)	98 Cf Californ. (251.079587)	99 Es Einstein. (252.08298)	100 Fm Fermium (257.065105)	101 Md Mendelev. (258.098431)	102 No Nobelium (259.1010)	103 Lr Lawrenc. (262.1066)
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1. PHYSICAL CONSTANTS

Table 1.1. Reviewed 2004 by P.J. Mohr and B.N. Taylor (NIST). Based mainly on the “CODATA Recommended Values of the Fundamental Physical Constants: 2002” by P.J. Mohr and B.N. Taylor, to be published in 2004. The last group of constants (beginning with the Fermi coupling constant) comes from the Particle Data Group. The figures in parentheses after the values give the 1-standard-deviation uncertainties in the last digits; the corresponding fractional uncertainties in parts per 10^9 (ppb) are given in the last column. This set of constants (aside from the last group) is recommended for international use by CODATA (the Committee on Data for Science and Technology). The full 2002 CODATA set of constants may be found at <http://physics.nist.gov/constants>

Quantity	Symbol, equation	Value	Uncertainty (ppb)
speed of light in vacuum	c	299 792 458 m s ⁻¹	exact [*]
Planck constant	h	6.626 0693(11) × 10 ⁻³⁴ J s	170
Planck constant, reduced	$\hbar \equiv h/2\pi$	1.054 571 68(18) × 10 ⁻³⁴ J s = 6.582 119 15(56) × 10 ⁻²² MeV s	170 85
electron charge magnitude	e	1.602 176 53(14) × 10 ⁻¹⁹ C = 4.803 204 41(41) × 10 ⁻¹⁰ esu	85, 85
conversion constant	hc	197.326 968(17) MeV fm	85
conversion constant	$(hc)^2$	0.389 379 323(67) GeV ² mbarn	170
electron mass	m_e	0.510 998 918(44) MeV/ c^2 = 9.109 3826(16) × 10 ⁻³¹ kg	86, 170
proton mass	m_p	938.272 029(80) MeV/ c^2 = 1.672 621 71(29) × 10 ⁻²⁷ kg = 1.007 276 466 88(13) u = 1836.152 672 61(85) m_e	86, 170 0.13, 0.46
deuteron mass	m_d	1875.612 82(16) MeV/ c^2	86
unified atomic mass unit (u)	(mass ¹² C atom)/12 = (1 g)/(N_A mol)	931.494 043(80) MeV/ c^2 = 1.660 538 86(28) × 10 ⁻²⁷ kg	86, 170
permittivity of free space	$\epsilon_0 = 1/\mu_0 c^2$	8.854 187 817 ... × 10 ⁻¹² F m ⁻¹	exact
permeability of free space	μ_0	4 π × 10 ⁻⁷ N A ⁻² = 12.566 370 614 ... × 10 ⁻⁷ N A ⁻²	exact
fine-structure constant	$\alpha = e^2/4\pi\epsilon_0\hbar c$	7.297 352 568(24) × 10 ⁻³ = 1/137.035 999 11(46) [†]	3.3, 3.3
classical electron radius	$r_e = e^2/4\pi\epsilon_0 m_e c^2$	2.817 940 325(28) × 10 ⁻¹⁵ m	10
(e^- Compton wavelength)/ 2π	$\lambda_e = h/m_e c = r_e \alpha^{-1}$	3.861 592 678(26) × 10 ⁻¹³ m	6.7
Bohr radius ($m_{\text{nucleus}} = \infty$)	$a_{\infty} = 4\pi\epsilon_0 \hbar^2 / m_e e^2 = r_e \alpha^{-2}$	0.529 177 2108(18) × 10 ⁻¹⁰ m	3.3
wavelength of 1 eV/c particle	$hc/(1 \text{ eV})$	1.239 841 91(11) × 10 ⁻⁶ m	85
Rydberg energy	$hcR_{\infty} = m_e e^4 / 2(4\pi\epsilon_0)^2 \hbar^2 = m_e c^2 \alpha^2 / 2$	13.605 6923(12) eV	85
Thomson cross section	$\sigma_T = 8\pi r_e^2 / 3$	0.665 245 873(13) barn	20
Bohr magneton	$\mu_B = eh/2m_e$	5.788 381 804(39) × 10 ⁻¹¹ MeV T ⁻¹	6.7
nuclear magneton	$\mu_N = eh/2m_p$	3.152 451 259(21) × 10 ⁻¹⁴ MeV T ⁻¹	6.7
electron cyclotron freq./field	$\omega_{\text{cycl}}^e / B = e/m_e$	1.758 820 12(15) × 10 ¹¹ rad s ⁻¹ T ⁻¹	86
proton cyclotron freq./field	$\omega_{\text{cycl}}^p / B = e/m_p$	9.578 833 76(82) × 10 ⁷ rad s ⁻¹ T ⁻¹	86
gravitational constant [‡]	G_N	6.6742(10) × 10 ⁻¹¹ m ³ kg ⁻¹ s ⁻² = 6.7087(10) × 10 ⁻³⁹ $\hbar c$ (GeV/ c^2) ⁻²	1.5 × 10 ⁵ 1.5 × 10 ⁵
standard gravitational accel.	g_n	9.806 65 m s ⁻²	exact
Avogadro constant	N_A	6.022 1415(10) × 10 ²³ mol ⁻¹	170
Boltzmann constant	k	1.380 6505(24) × 10 ⁻²³ J K ⁻¹ = 8.617 343(15) × 10 ⁻⁵ eV K ⁻¹	1800 1800
molar volume, ideal gas at STP	$N_A k(273.15 \text{ K})/(101 325 \text{ Pa})$	22.413 996(39) × 10 ⁻³ m ³ mol ⁻¹	1700
Wien displacement law constant	$b = \lambda_{\text{max}} T$	2.897 7685(51) × 10 ⁻³ m K	1700
Stefan-Boltzmann constant	$\sigma = \pi^2 k^4 / 60 \hbar^3 c^2$	5.670 400(40) × 10 ⁻⁸ W m ⁻² K ⁻⁴	7000
Fermi coupling constant ^{**}	$G_F / (\hbar c)^3$	1.166 37(1) × 10 ⁻⁵ GeV ⁻²	9000
weak-mixing angle	$\sin^2 \hat{\theta}(M_Z)$ ($\overline{\text{MS}}$)	0.23120(15) ^{††}	6.5 × 10 ⁵
W^\pm boson mass	m_W	80.425(38) GeV/ c^2	4.8 × 10 ⁵
Z^0 boson mass	m_Z	91.1876(21) GeV/ c^2	2.3 × 10 ⁴
strong coupling constant	$\alpha_s(m_Z)$	0.1187(20)	1.7 × 10 ⁷
$\pi = 3.141 592 653 589 793 238$ $e = 2.718 281 828 459 045 235$ $\gamma = 0.577 215 664 901 532 861$			
1 m \equiv 0.0254 m	1 G \equiv 10 ⁻⁴ T	1 eV = 1.602 176 53(14) × 10 ⁻¹⁹ J	kT at 300 K = [38.681 684(68)] ⁻¹ eV
1 Å \equiv 0.1 nm	1 dyne \equiv 10 ⁻⁵ N	1 eV/ c^2 = 1.782 661 81(15) × 10 ⁻³⁶ kg	0 °C \equiv 273.15 K
1 barn \equiv 10 ⁻²⁸ m ²	1 erg \equiv 10 ⁻⁷ J	2.997 924 58 × 10 ⁹ esu = 1 C	1 atmosphere \equiv 760 Torr \equiv 101 325 Pa

^{*} The meter is the length of the path traveled by light in vacuum during a time interval of 1/299 792 458 of a second.

[†] At $Q^2 = 0$. At $Q^2 \approx m_W^2$ the value is $\sim 1/128$.

[‡] Absolute lab measurements of G_N have been made only on scales of about 1 cm to 1 m.

^{**} See the discussion in Sec. 10, “Electroweak model and constraints on new physics.”

^{††} The corresponding $\sin^2 \theta$ for the effective angle is 0.23149(15).

3. INTERNATIONAL SYSTEM OF UNITS (SI)

See “The International System of Units (SI),” NIST Special Publication **330**, B.N. Taylor, ed. (USGPO, Washington, DC, 1991); and “Guide for the Use of the International System of Units (SI),” NIST Special Publication **811**, 1995 edition, B.N. Taylor (USGPO, Washington, DC, 1995).

<u>SI prefixes</u>		
10^{24}	yotta	(Y)
10^{21}	zetta	(Z)
10^{18}	exa	(E)
10^{15}	peta	(P)
10^{12}	tera	(T)
10^9	giga	(G)
10^6	mega	(M)
10^3	kilo	(k)
10^2	hecto	(h)
10	deca	(da)
10^{-1}	deci	(d)
10^{-2}	centi	(c)
10^{-3}	milli	(m)
10^{-6}	micro	(μ)
10^{-9}	nano	(n)
10^{-12}	pico	(p)
10^{-15}	femto	(f)
10^{-18}	atto	(a)
10^{-21}	zepto	(z)
10^{-24}	yocto	(y)

2 3. International system of units (SI)

Physical quantity	Name of unit	Symbol
<i>Base units</i>		
length	meter	m
mass	kilogram	kg
time	second	s
electric current	ampere	A
thermodynamic temperature	kelvin	K
amount of substance	mole	mol
luminous intensity	candela	cd
<i>Derived units with special names</i>		
plane angle	radian	rad
solid angle	steradian	sr
frequency	hertz	Hz
energy	joule	J
force	newton	N
pressure	pascal	Pa
power	watt	W
electric charge	coulomb	C
electric potential	volt	V
electric resistance	ohm	Ω
electric conductance	siemens	S
electric capacitance	farad	F
magnetic flux	weber	Wb
inductance	henry	H
magnetic flux density	tesla	T
luminous flux	lumen	lm
illuminance	lux	lx
celsius temperature	degree celsius	$^{\circ}\text{C}$
activity (of a radioactive source)*	becquerel	Bq
absorbed dose (of ionizing radiation)*	gray	Gy
dose equivalent*	sievert	Sv

1.1: Introductory Concepts

- Review of quantum mechanical postulates
- Consider a system of a single moving particle

Postulate I: The system can be described by a wave function or state function

$$\Psi(x, y, z, t)$$

which is bounded, single-valued, continuous, with continuous partial derivatives

$$\frac{\partial \Psi}{\partial x}$$

Postulate IV: The wave function must obey the Schrödinger Time-Dependent Wave Equation:

$$\hat{H}\Psi = -\frac{\hbar}{i} \frac{\partial \Psi}{\partial t}$$

where $\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z, t)$

Hamiltonian

Kinetic Energy

Potential Energy

$$\nabla^2 = \vec{\nabla} \cdot \vec{\nabla} = \left(\hat{i} \frac{\partial}{\partial x} + \hat{j} \frac{\partial}{\partial y} + \hat{k} \frac{\partial}{\partial z} \right) \cdot \left(\hat{i} \frac{\partial}{\partial x} + \hat{j} \frac{\partial}{\partial y} + \hat{k} \frac{\partial}{\partial z} \right) = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$$

If the particle is bound; that is, exists somewhere in space:

$$\longrightarrow \iiint \Psi^*(x, y, z, t) \Psi(x, y, z, t) dx dy dz = C = \int \Psi^* \Psi d\tau$$

C is a real constant.

Therefore, can normalize the wave function. Multiply by a real or imaginary constant N such that:

$$\Phi = N\Psi \text{ so that } \int \Phi^* \Phi d\tau = 1$$

$$\begin{aligned} \longrightarrow \int \Phi^* \Phi d\tau &= \int (N\Psi)^* (N\Psi) d\tau = N^* N \int \Psi^* \Psi d\tau \\ &= N^* N C = 1 \Rightarrow N^* N = \frac{1}{C} \text{ or } N = \frac{1}{\sqrt{C}} e^{i\delta} \end{aligned}$$

$e^{i\delta}$ is an arbitrary phase factor. Can choose $\delta = 0$

-If particle is unbound, not localized (e.g. beam problems in C374a)

$$\therefore \int \Psi^* \Psi d\tau = \infty$$

Postulate II: $\Psi^* \Psi = |\Psi(\vec{r}, t)|^2$ is the Probability Distribution

Recall:

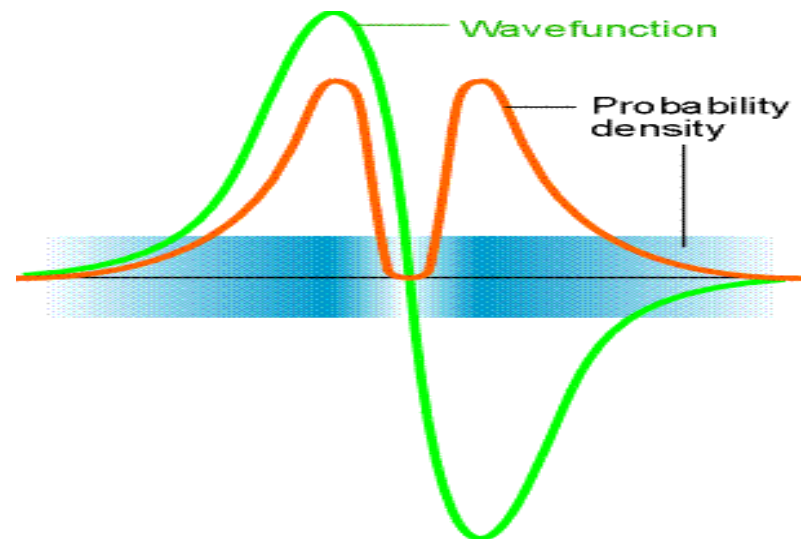
$$\begin{aligned} & (a + ib)^*(a + ib) \\ &= (a - ib)(a + ib) \\ &= a^2 - aib + aib - (ib)^2 \quad \text{A real number} \\ &= a^2 + b^2 \end{aligned}$$



Max Born)

$|\Psi(x, y, z, t)|^2 dx dy dz$ is the probability that the particle can be found between x and $x+dx$, y and $y+dy$, and z and $z+dz$, at time $=t$

$\int \Psi^* \Psi d\tau = 1$ means there is a 100% probability of finding the particle somewhere at time $= t$.



Postulate V: Any real physical observable parameter of the system, M , is calculated as:

$$\overline{M} = \langle M \rangle = \frac{\int \Psi^* \hat{M} \Psi d\tau}{\int \Psi^* \Psi d\tau} = \int \Psi^* \hat{M} \Psi d\tau$$

use if Ψ is
not normalized

Use if Ψ is
normalized

\overline{M} = expectation or average value = value one would observe if a large number of measurements of M were made and averaged while in Ψ .

Postulate III: \hat{M} is the quantum mechanical operator generated according to the following rules:

classical	quantum
x, y, z, t, \vec{r}	x, y, z, t, \vec{r}
$\vec{p} = \hat{i}p_x + \hat{j}p_y + \hat{k}p_z$	$\hat{p} = \hat{i}\frac{\hbar}{i}\frac{\partial}{\partial x} + \hat{j}\frac{\hbar}{i}\frac{\partial}{\partial y} + \hat{k}\frac{\hbar}{i}\frac{\partial}{\partial z}$

so $M(x, y, z, t, p_x, p_y, p_z) \rightarrow \hat{M}(x, y, z, t, \hat{p}_x, \hat{p}_y, \hat{p}_z)$

Thus:
$$H = T + V \rightarrow \hat{H} = \hat{T} + \hat{V}$$

Assume \hat{V} is a function of x, y, z, t only. Therefore $\hat{V} = V$

Know
$$T = \frac{1}{2m} \vec{p} \cdot \vec{p} \Rightarrow \hat{T} = \frac{1}{2m} \hat{\vec{p}} \cdot \hat{\vec{p}} = \frac{1}{2m} \left(\frac{\hbar}{i} \vec{\nabla} \right) \cdot \left(\frac{\hbar}{i} \vec{\nabla} \right) = -\frac{\hbar^2}{2m} \nabla^2$$

(as earlier)

Postulate IV: It is possible for the operator to regenerate the wave function within a constant; that is:

$$\hat{M}\Psi = m\Psi$$

Here Ψ is an **eigenfunction** (“self” function) and m is the **eigenvalue** of the operator

This means that the expectation value is precisely determined.

$$\bar{M} = \frac{\int \Psi^* \hat{M} \Psi d\tau}{\int \Psi^* \Psi d\tau} = \frac{\int \Psi^* m \Psi d\tau}{\int \Psi^* \Psi d\tau} = m \frac{\int \Psi^* \Psi d\tau}{\int \Psi^* \Psi d\tau} = m$$

Procedure

A: Solve the Schrödinger Equation to get a set of wave functions Ψ_k , which also provides a set of quantum numbers, k

(e.g.: H-atom \rightarrow polynomials $R_{n,l} Y_l^m$ with three sets of quantum numbers: n, l, m)

The set of wave functions describe all the possible states of the system = state functions

B: Use the wave functions to calculate expectation values for a particular state of interest; for example, the energy E .