(20%)1 Define and illustrate the followings:

(a)orbital angular momentum

(b) quantum

(c)the uncertainty principle

(d) blackbody radiation

(e)two examples for wave and particle properties of a matter

(f) Born interpretation of the wave function

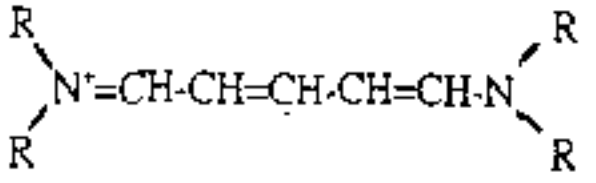
(g) $E_n=(n^2h^2)/(8mL^2)$ for a particle in one-dimension box ,why is $n\neq 0$?

(h) zero-point energy

(i) degeneracy

(j) Frank-Condon principle

(15%)2.An organic dye molecule has the structure as



involving a series of conjugated double bonds . This is similar to the quantum mechanical problem of a electron in a two nitrogen box where the potential energy is zero inside the box and rises to infinity at the two nitrogen walls . The length of the box here is L , the distance between the two nitrogen atoms.

(a) Derive the formula $E_n=(n^2h^2)/(8mL^2)$ for the energy levels of an electron in such a box of length L (one-dimensional), starting from the Schrodinger equation.

(b) Draw an energy level diagram showing the five lowest energy states with their respective quantum numbers n , and sketch the associated wave functions.

(c)The six Π electrons occupy the lowest energy states (subject to the Pauli Excusion Principle).Indicate on your energy level diagram where the electrons would be.

(d) Light absorption raises an electron from the highest filled energy level to the lowest unfilled level. Compute the energy difference between these levels, and the wave length in nanometers of the absorbed light . For this you need to know L , which is 0.84nm.

(e)How much will the wavelength increase for a dye containing one additional vinylene group, -CH=CH-, for which L is increased by about 0.14nm.

(5%)3. Sketch the proton NMR spectrum of $CHCl_2$-CH_2Cl:

(a)at low resolution , giving relative intensities of peaks

(b) at resolution adequate to show the spin-spin splitting,indicating relative intensities of peaks.

(15%)4.The following lines were observed in the vibration-rotational bands of the infrared spectrum (R and P branches) of HI, in decreasing order of $\overline{\nu}$ in cm^{-1} : 2288.5 , 2277.5 ,2266.1 , 2254.3 , 2242.2 , 2216.7 , 2203.6 , 2190.0 , 2176.0 , 2161.7 , 2147.5 , 2132.7 , 2117.7 . Calculate

(a) the rotational constants in the lowest and first excited vibrational states:

(b) the moments of inertia in the two states

(c) the internuclear distances in the two states:

(d) the origin of the fundamental band:

(e) the force constant of the H-I bond:

(5%)5.By means of the concept of hybrid bond orbitals , predict the structure of CH_3.Discuss the probable microwave and infrared spectra of this molecule.

(10%)6.List the symmetry elements and derive the point group for each of the following molecules: CCl_4 , $CHCl_3$, CH_2Cl_2, CH_3Cl , C_2H_5Cl (in various conformations)

(10%)7.What kind of hybridization will explain the following molecular geometries:

(a)SF_6,octahedral

(b) $Au(CN)_2^-$ square planar

(c)NO_3^-,trigonal planar

(d) CH_4,tetragonal

(10%)8.compare the molecules OF , OF^-, OF^+ ,discussing molecular orbitals ,bond order, bond lengths , bond energies , and paramagnetism .

(10%)9.Draw reasonable potential-energy curves for ground and excited states that on the basis of the Franck-Condon principle will provide a reasonable explanation of the following observations

(a) A molecule has a $\nu'=0$ to $\nu''=0$ transition as the most intense band in its emission spectrum .

(b) A molecule has a broad structureless absorption band but its emission spectrum is quite sharp and has fine structure .

Fundamental Constants*

Quantity	Symbol	SI value	cgs or other value	Uncertainty[b]
Avogadro constant	N_A, L	6.022045×10^{23} mol^{-1}		31
Boltzmann constant	k	1.380662×10^{-23} J K^{-1}	1.380662×10^{-16} erg K^{-1}	44
Speed of light in vacuum	c	2.99792458×10^{8} m s^{-1}	$2.99792458 \times 10^{10}$ cm s^{-1}	1.2
Electron rest mass	m_e	9.109534×10^{-31} kg	9.109534×10^{-28} g	47
Proton rest mass	m_p	$1.6726485 \times 10^{-27}$ kg	$1.6726485 \times 10^{-24}$ g	86
Elementary charge	e	$1.6021892 \times 10^{-19}$ C	$1.6021892 \times 10^{-20}$ emu	46
			4.803242×10^{-10} esu	14
Planck constant	h	6.626176×10^{-34} J s	6.626176×10^{-27} erg s	36
Faraday constant	F	9.648456×10^{4} C mol^{-1}		27
Permeability of vacuum	μ_0	$4\pi \times 10^{-7}$ H m^{-1}		
Permittivity of vacuum	ϵ_0	$8.854187818 \times 10^{-12}$ F m^{-1}		71
Rydberg constant	R_∞	$1.097373177 \times 10^{7}$ m^{-1}	$1.097373177 \times 10^{5}$ cm^{-1}	83
Bohr radius	a_0	$5.2917706 \times 10^{-11}$ m	5.2917706×10^{-9} cm	44
Bohr magneton	μ_B	9.274078×10^{-24} J T^{-1}	9.274078×10^{-21} erg G^{-1}	36
Nuclear magneton	μ_N	5.050824×10^{-27} J T^{-1}	5.050824×10^{-24} erg G^{-1}	20
Gravitational constant	G	6.6720×10^{-11} m^3 s^{-2} kg^{-1}	6.6720×10^{-8} cm^3 s^{-2} g^{-1}	41
Molar volume of ideal gas at STP	V_m	22.41383×10^{-3} m^3 mol^{-1}	22.41383×10^{3} cm^3 mol^{-1}	70
Molar gas constant	R	8.31441 J mol^{-1} K^{-1}	8.31441×10^{7} erg mol^{-1} K^{-1}	26
			82.0568 cm^3 atm mol^{-1} K^{-1}	26

[a] Adapted from the least squares adjusted values of E. R. Cohen and B. N. Taylor, *J. Phys. Chem. Ref. Data* 2, 663 (1973). Unit abbreviations used are as follows: C = coulomb; F = farad; G = gauss; H = henry; J = joule; K = kelvin; T = tesla (10^4 G); note that for the last entry 1 atm = 101325 Pa (pascal = N m^{-2}).

[b] The numbers in this column list the one standard deviation uncertainties in the last digits of the indicated values. In terms of accuracy in parts per million (ppm) the most accurate constant is c, which is known to within 0.004 ppm (ϵ_0 which is defined as $1/\mu_0 c^2$ thus has an accuracy of 0.008 ppm. R_∞ is known to within 0.075 ppm, and a_0 to within 0.82 ppm. The constants associated with molar volumes (k, V_m, and R) are known to about 31 ppm. The uncertainties of the remaining listed constants are in the range 3–6 ppm, except for the gravitational constant G, whose uncertainty of 515 ppm is very much larger than all the other fundamental constants.

Note: It may be of some interest to note the values of some of these constants as they were known in 1941. Omitting the units and exponent factors, and placing the 1941 uncertainties in parentheses, these were: c = 2.99776 (4); G = 6.670 (5); e = 1.60203 (33); R_∞ = 1.09737303 (17); h = 6.6242 (24); k = 1.38047 (26); m_e = 9.1066 (32). It is difficult to compare 1941 and present values for quantities involving moles and molar masses in view of the chemical and physical scales which existed side by side in 1941. Some 1963 values are: e = 1.60210 (2); h = 6.62559 (16); m_e = 9.10908 (13); N_A = 6.02252 (9); F = 9.64870 (6). The values do change over time.

Conversion Factors

1 atm = 1.01325×10^5 N m^{-2}
= 1.01325×10^5 Pa (pascal)

1 torr = $\frac{1}{760}$ atm

1 inch = 2.5400. . . cm
1 ft = 30.48 cm
1 mile = 1609.3 m
1 Å = 10^{-8} cm
1 liter = 1000.028 cm^3
1 dyn = 10^{-5} N
1 erg = 1 dyn cm = 10^{-7} J

1 cal = 4.184000. . . J
1 eV = 1.6022×10^{-19} J

1 Btu = 1054 J

1 hp = 746 W
1 D (debye) = 3.338×10^{-30} m C
1 poise = 0.1 kg m^{-1} s^{-1}
gas constant R = 8.3144 J mol^{-1} K^{-1}
= 82.057 cm^3 atm mol^{-1} K^{-1}
= 1.9872 cal mol^{-1} K^{-1}

SI Prefixes

Multiple or submultiple	Prefix	Symbol	Multiple or submultiple	Prefix	Symbol
10^{12}	tera	T	10^{-3}	milli	m
10^{9}	giga	G	10^{-6}	micro	μ
10^{6}	mega	M	10^{-9}	nano	n
10^{3}	kilo	k	10^{-12}	pico	p
10^{-1}	deci[a]	d	10^{-15}	femto	f
10^{-2}	centi[a]	c	10^{-18}	atto	a

[a] The centi- and deci- prefixes are retained for historical reasons. The centimeter is still commonly used. The use of the "liter" is still strongly entrenched in scientific usage, and the prefix deci- allows one to call the liter the cubic decimeter. The retention of deci- and centi- is anachronistic in the new SI system, and their use may diminish over the next several decades.

Atomic Masses and Numbers

Name	Symbol	Atomic number	Atomic mass	Name	Symbol	Atomic number	Atomic mass
Actinium	Ac	89	227.0278	Molybdenum	Mo	42	95.94
Aluminum	Al	13	26.98154	Neodymium	Nd	60	144.24
Americium	Am	95	(243)	Neon	Ne	10	20.179
Antimony	Sb	51	121.75	Neptunium	Np	93	237.0482
Argon	Ar	18	39.948	Nickel	Ni	28	58.70
Arsenic	As	33	74.9216	Niobium	Nb	41	92.9064
Astatine	At	85	(210)	Nitrogen	N	7	14.0067
Barium	Ba	56	137.33	Nobelium	No	102	(259)
Berkelium	Bk	97	(247)	Osmium	Os	76	190.2
Beryllium	Be	4	9.01218	Oxygen	O	8	15.9994
Bismuth	Bi	83	208.9804	Palladium	Pd	46	106.4
Boron	B	5	10.81	Phosphorus	P	15	30.97376
Bromine	Br	35	79.904	Platinum	Pt	78	195.09
Cadmium	Cd	48	112.41	Plutonium	Pu	94	(244)
Caesium	Cs	55	132.9054	Polonium	Po	84	(209)
Calcium	Ca	20	40.08	Potassium	K	19	39.0983
Californium	Cf	98	(251)	Praseodymium	Pr	59	140.9077
Carbon	C	6	12.011	Promethium	Pm	61	(145)
Cerium	Ce	58	140.12	Protactinium	Pa	91	231.0359
Chlorine	Cl	17	35.453	Radium	Ra	88	226.0254
Chromium	Cr	24	51.996	Radon	Rn	86	(222)
Cobalt	Co	27	58.9332	Rhenium	Re	75	186.207
Copper	Cu	29	63.546	Rhodium	Rh	45	102.9055
Curium	Cm	96	(247)	Rubidium	Rb	37	85.4678
Dysprosium	Dy	66	162.50	Ruthenium	Ru	44	101.07
Einsteinium	Es	99	(252)	Samarium	Sm	62	150.4
Erbium	Er	68	167.26	Scandium	Sc	21	44.9559
Europium	Eu	63	151.96	Selenium	Se	34	78.96
Fermium	Fm	100	(257)	Silicon	Si	14	28.0855
Fluorine	F	9	18.998403	Silver	Ag	47	107.868
Francium	Fr	87	(223)	Sodium	Na	11	22.98977
Gadolinium	Gd	64	157.25	Strontium	Sr	38	87.62
Gallium	Ga	31	69.72	Sulfur	S	16	32.06
Germanium	Ge	32	72.59	Tantalum	Ta	73	180.9479
Gold	Au	79	196.9665	Technetium	Tc	43	(98)
Hafnium	Hf	72	178.49	Tellurium	Te	52	127.60
Helium	He	2	4.00260	Terbium	Tb	65	158.9254
Holmium	Ho	67	164.9304	Thallium	Tl	81	204.37
Hydrogen	H	1	1.0079	Thorium	Th	90	232.0381
Indium	In	49	114.82	Thulium	Tm	69	168.9342
Iodine	I	53	126.9045	Tin	Sn	50	118.69
Iridium	Ir	77	192.22	Titanium	Ti	22	47.90
Iron	Fe	26	55.847	Tungsten (Wolfram)	W	74	183.85
Krypton	Kr	36	83.80	(Unnilhexium)	(Unh)	106	(263)
Lanthanum	La	57	138.9055	(Unnilpentium)	(Unp)	105	(262)
Lawrencium	Lr	103	(260)	(Unnilquadium)	(Unq)	104	(261)
Lead	Pb	82	207.2	Uranium	U	92	238.029
Lithium	Li	3	6.941	Vanadium	V	23	50.9415
Lutetium	Lu	71	174.967	Xenon	Xe	54	131.30
Magnesium	Mg	12	24.305	Ytterbium	Yb	70	173.04
Manganese	Mn	25	54.9380	Yttrium	Y	39	88.9059
Mendelevium	Md	101	(258)	Zinc	Zn	30	65.38
Mercury	Hg	80	200.59	Zirconium	Zr	40	91.22

Source: Adapted from *Pure Appl. Chem.* 51, 405 (1979). Values in parentheses are for nonnaturally occurring elements and are the mass numbers of the longest lived isotope of the element.