

EXAM INFORMATION

Radial Distribution Function: $P(r) \equiv RDF(r) \equiv Br^2 R(r)^2$
B is the normalization constant.

p² Operator: $\hat{p}^2 = -\hbar^2 \frac{d^2}{dx^2}$

Heisenberg Uncertainty Principle: $\sigma_x \sigma_p \geq \frac{\hbar}{2}$

Integrals: $\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$

Particle in a Box

Energy Levels: $E_n = \frac{n^2 \hbar^2}{8ma^2} \quad n = 1, 2, 3 \dots$

Harmonic Oscillator

Energy Levels and Frequency: $E_n = \left(n + \frac{1}{2}\right) \hbar \omega \quad n = 0, 1, 2, \dots \quad \omega = \sqrt{\frac{k}{\mu}} = 2\pi\nu = 2\pi c\tilde{\nu} \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$

Rigid Rotor

Energy Levels: $E_J = \frac{\hbar^2}{8\pi^2 I} J(J+1) = hc\tilde{B}J(J+1) \quad \tilde{B} = \frac{h}{8\pi^2 Ic} \quad J = 0, 1, 2, \dots \quad g_J = 2J+1$

Moment of Inertia: Linear Polyatomic: $I = \sum m_i r_i^2$ **Diatomic:** $I = \mu r^2 \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$

Quadratic Equation: $ax^2 + bx + c = 0 \quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Thermodynamics: $\Delta G^0 = -RT \ln(K_{eq}) = \Delta H^0 - T\Delta S^0$
This equation is not needed on this year's exam

EXAM INFORMATION (CONT'D)

π **Electron Charge:** $q_{\mu} \equiv \sum_i^{orbs} n_i c_{i\mu}^2$

π **Bond Order:** $p_{\mu\nu} \equiv \sum_i^{orbs} n_i c_{i\mu} c_{i\nu}$

Transition Moment: $M_{0i} = M_{0i}^x \vec{i} + M_{0i}^y \vec{j} + M_{0i}^z \vec{k}$

$$M_{0i}^x = e \langle \Psi_i | x | \Psi_0 \rangle$$

$$M_{0i}^y = e \langle \Psi_i | y | \Psi_0 \rangle$$

$$M_{0i}^z = e \langle \Psi_i | z | \Psi_0 \rangle$$

C_{2h} Character Table

C _{2h}	E	C ₂	i	σ_h	
A _g	1	1	1	1	x ² , y ² , z ² , xy
B _g	1	-1	1	-1	xz, yz
A _u	1	1	-1	-1	z
B _u	1	-1	-1	1	x, y

Constants and Conversions:

$$h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$\hbar = h/2\pi = 1.05 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$k = 1.38 \times 10^{-23} \text{ J/K}$$

$$c = 3.00 \times 10^8 \text{ m/s} = 3.00 \times 10^{10} \text{ cm/s}$$

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$$

$$m_e = 9.10 \times 10^{-31} \text{ kg}$$

$$m_p = 1.67 \times 10^{-27} \text{ kg}$$

$$1 \text{ \AA} = 10^{-10} \text{ m}$$

$$1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$$

$$1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$$

$$1 \text{ J} = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2$$

$$1 \text{ N} = 1 \text{ kg}\cdot\text{m}/\text{s}^2$$

$$1 \text{ hartree (au)} = 27.21 \text{ eV}$$

PERIODIC TABLE OF THE ELEMENTS

1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIII	9 VIII	10 VIII	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																									
1 H 1.008	3 Li 6.941	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3	55 Cs 132.9	56 Ba 137.3	57 Fr (223)	58 Ra 226.0	59 La 138.9	60 Ce 140.1	61 Pr 140.9	62 Nd 144.2	63 Pm (145)	64 Sm 150.4	65 Eu 152.0	66 Gd 157.2	67 Tb 158.9	68 Dy 162.5	69 Ho 164.9	70 Er 167.3	71 Tm 168.9	72 Yb 173.0	73 Ac 227.0	74 Th 232.0	75 Pa 231.0	76 U 238.0	77 Np 237.0	78 Pu (244)	79 Am (243)	80 Cm (247)	81 Bk (247)	82 Cf (251)	83 Es (252)	84 Fm (257)	85 Md (258)	86 No (259)	87 Fr (223)	88 Ra 226.0	89 La 138.9	90 Ce 140.1	91 Pr 140.9	92 Nd 144.2	93 Pm (145)	94 Sm 150.4	95 Eu 152.0	96 Gd 157.2	97 Tb 158.9	98 Dy 162.5	99 Ho 164.9	100 Er 167.3	101 Tm 168.9	102 Yb 173.0	103 Ac 227.0	104 Th 232.0	105 Pa 231.0	106 U 238.0	107 Np 237.0	108 Pu (244)	109 Am (243)	110 Cm (247)	111 Bk (247)	112 Cf (251)	113 Es (252)	114 Fm (257)	115 Md (258)	116 No (259)	117 Fr (223)	118 Ra 226.0	119 La 138.9	120 Ce 140.1	121 Pr 140.9	122 Nd 144.2	123 Pm (145)	124 Sm 150.4	125 Eu 152.0	126 Gd 157.2	127 Tb 158.9	128 Dy 162.5	129 Ho 164.9	130 Er 167.3	131 Tm 168.9	132 Yb 173.0	133 Ac 227.0	134 Th 232.0	135 Pa 231.0	136 U 238.0	137 Np 237.0	138 Pu (244)	139 Am (243)	140 Cm (247)	141 Bk (247)	142 Cf (251)	143 Es (252)	144 Fm (257)	145 Md (258)	146 No (259)	147 Fr (223)	148 Ra 226.0	149 La 138.9	150 Ce 140.1	151 Pr 140.9	152 Nd 144.2	153 Pm (145)	154 Sm 150.4	155 Eu 152.0	156 Gd 157.2	157 Tb 158.9	158 Dy 162.5	159 Ho 164.9	160 Er 167.3	161 Tm 168.9	162 Yb 173.0	163 Ac 227.0	164 Th 232.0	165 Pa 231.0	166 U 238.0	167 Np 237.0	168 Pu (244)	169 Am (243)	170 Cm (247)	171 Bk (247)	172 Cf (251)	173 Es (252)	174 Fm (257)	175 Md (258)	176 No (259)	177 Fr (223)	178 Ra 226.0	179 La 138.9	180 Ce 140.1	181 Pr 140.9	182 Nd 144.2	183 Pm (145)	184 Sm 150.4	185 Eu 152.0	186 Gd 157.2	187 Tb 158.9	188 Dy 162.5	189 Ho 164.9	190 Er 167.3	191 Tm 168.9	192 Yb 173.0	193 Ac 227.0	194 Th 232.0	195 Pa 231.0	196 U 238.0	197 Np 237.0	198 Pu (244)	199 Am (243)	200 Cm (247)	201 Bk (247)	202 Cf (251)	203 Es (252)	204 Fm (257)	205 Md (258)	206 No (259)	207 Fr (223)	208 Ra 226.0	209 La 138.9	210 Ce 140.1	211 Pr 140.9	212 Nd 144.2	213 Pm (145)	214 Sm 150.4	215 Eu 152.0	216 Gd 157.2	217 Tb 158.9	218 Dy 162.5	219 Ho 164.9	220 Er 167.3	221 Tm 168.9	222 Yb 173.0	223 Ac 227.0	224 Th 232.0	225 Pa 231.0	226 U 238.0	227 Np 237.0	228 Pu (244)	229 Am (243)	230 Cm (247)	231 Bk (247)	232 Cf (251)	233 Es (252)	234 Fm (257)	235 Md (258)	236 No (259)	237 Fr (223)	238 Ra 226.0	239 La 138.9	240 Ce 140.1	241 Pr 140.9	242 Nd 144.2	243 Pm (145)	244 Sm 150.4	245 Eu 152.0	246 Gd 157.2	247 Tb 158.9	248 Dy 162.5	249 Ho 164.9	250 Er 167.3	251 Tm 168.9	252 Yb 173.0	253 Ac 227.0	254 Th 232.0	255 Pa 231.0	256 U 238.0	257 Np 237.0	258 Pu (244)	259 Am (243)	260 Cm (247)	261 Bk (247)	262 Cf (251)	263 Es (252)	264 Fm (257)	265 Md (258)	266 No (259)	267 Fr (223)	268 Ra 226.0	269 La 138.9	270 Ce 140.1	271 Pr 140.9	272 Nd 144.2	273 Pm (145)	274 Sm 150.4	275 Eu 152.0	276 Gd 157.2	277 Tb 158.9	278 Dy 162.5	279 Ho 164.9	280 Er 167.3	281 Tm 168.9	282 Yb 173.0	283 Ac 227.0	284 Th 232.0	285 Pa 231.0	286 U 238.0	287 Np 237.0	288 Pu (244)	289 Am (243)	290 Cm (247)	291 Bk (247)	292 Cf (251)	293 Es (252)	294 Fm (257)	295 Md (258)	296 No (259)	297 Fr (223)	298 Ra 226.0	299 La 138.9	300 Ce 140.1	301 Pr 140.9	302 Nd 144.2	303 Pm (145)	304 Sm 150.4	305 Eu 152.0	306 Gd 157.2	307 Tb 158.9	308 Dy 162.5	309 Ho 164.9	310 Er 167.3	311 Tm 168.9	312 Yb 173.0	313 Ac 227.0	314 Th 232.0	315 Pa 231.0	316 U 238.0	317 Np 237.0	318 Pu (244)	319 Am (243)	320 Cm (247)	321 Bk (247)	322 Cf (251)	323 Es (252)	324 Fm (257)	325 Md (258)	326 No (259)	327 Fr (223)	328 Ra 226.0	329 La 138.9	330 Ce 140.1	331 Pr 140.9	332 Nd 144.2	333 Pm (145)	334 Sm 150.4	335 Eu 152.0	336 Gd 157.2	337 Tb 158.9	338 Dy 162.5	339 Ho 164.9	340 Er 167.3	341 Tm 168.9	342 Yb 173.0	343 Ac 227.0	344 Th 232.0	345 Pa 231.0	346 U 238.0	347 Np 237.0	348 Pu (244)	349 Am (243)	350 Cm (247)	351 Bk (247)	352 Cf (251)	353 Es (252)	354 Fm (257)	355 Md (258)	356 No (259)	357 Fr (223)	358 Ra 226.0	359 La 138.9	360 Ce 140.1	361 Pr 140.9	362 Nd 144.2	363 Pm (145)	364 Sm 150.4	365 Eu 152.0	366 Gd 157.2	367 Tb 158.9	368 Dy 162.5	369 Ho 164.9	370 Er 167.3	371 Tm 168.9	372 Yb 173.0	373 Ac 227.0	374 Th 232.0	375 Pa 231.0	376 U 238.0	377 Np 237.0	378 Pu (244)	379 Am (243)	380 Cm (247)	381 Bk (247)	382 Cf (251)	383 Es (252)	384 Fm (257)	385 Md (258)	386 No (259)	387 Fr (223)	388 Ra 226.0	389 La 138.9	390 Ce 140.1	391 Pr 140.9	392 Nd 144.2	393 Pm (145)	394 Sm 150.4	395 Eu 152.0	396 Gd 157.2	397 Tb 158.9	398 Dy 162.5	399 Ho 164.9	400 Er 167.3	401 Tm 168.9	402 Yb 173.0	403 Ac 227.0	404 Th 232.0	405 Pa 231.0	406 U 238.0	407 Np 237.0	408 Pu (244)	409 Am (243)	410 Cm (247)	411 Bk (247)	412 Cf (251)	413 Es (252)	414 Fm (257)	415 Md (258)	416 No (259)	417 Fr (223)	418 Ra 226.0	419 La 138.9	420 Ce 140.1	421 Pr 140.9	422 Nd 144.2	423 Pm (145)	424 Sm 150.4	425 Eu 152.0	426 Gd 157.2	427 Tb 158.9	428 Dy 162.5	429 Ho 164.9	430 Er 167.3	431 Tm 168.9	432 Yb 173.0	433 Ac 227.0	434 Th 232.0	435 Pa 231.0	436 U 238.0	437 Np 237.0	438 Pu (244)	439 Am (243)	440 Cm (247)	441 Bk (247)	442 Cf (251)	443 Es (252)	444 Fm (257)	445 Md (258)	446 No (259)	447 Fr (223)	448 Ra 226.0	449 La 138.9	450 Ce 140.1	451 Pr 140.9	452 Nd 144.2	453 Pm (145)	454 Sm 150.4	455 Eu 152.0	456 Gd 157.2	457 Tb 158.9	458 Dy 162.5	459 Ho 164.9	460 Er 167.3	461 Tm 168.9	462 Yb 173.0	463 Ac 227.0	464 Th 232.0	465 Pa 231.0	466 U 238.0	467 Np 237.0	468 Pu (244)	469 Am (243)	470 Cm (247)	471 Bk (247)	472 Cf (251)	473 Es (252)	474 Fm (257)	475 Md (258)	476 No (259)	477 Fr (223)	478 Ra 226.0	479 La 138.9	480 Ce 140.1	481 Pr 140.9	482 Nd 144.2	483 Pm (145)	484 Sm 150.4	485 Eu 152.0	486 Gd 157.2	487 Tb 158.9	488 Dy 162.5	489 Ho 164.9	490 Er 167.3	491 Tm 168.9	492 Yb 173.0	493 Ac 227.0	494 Th 232.0	495 Pa 231.0	496 U 238.0	497 Np 237.0	498 Pu (244)	499 Am (243)	500 Cm (247)	501 Bk (247)	502 Cf (251)	503 Es (252)	504 Fm (257)	505 Md (258)	506 No (259)	507 Fr (223)	508 Ra 226.0	509 La 138.9	510 Ce 140.1	511 Pr 140.9	512 Nd 144.2	513 Pm (145)	514 Sm 150.4	515 Eu 152.0	516 Gd 157.2	517 Tb 158.9	518 Dy 162.5	519 Ho 164.9	520 Er 167.3	521 Tm 168.9	522 Yb 173.0	523 Ac 227.0	524 Th 232.0	525 Pa 231.0	526 U 238.0	527 Np 237.0	528 Pu (244)	529 Am (243)	530 Cm (247)	531 Bk (247)	532 Cf (251)	533 Es (252)	534 Fm (257)	535 Md (258)	536 No (259)	537 Fr (223)	538 Ra 226.0	539 La 138.9	540 Ce 140.1	541 Pr 140.9	542 Nd 144.2	543 Pm (145)	544 Sm 150.4	545 Eu 152.0	546 Gd 157.2	547 Tb 158.9	548 Dy 162.5	549 Ho 164.9	550 Er 167.3	551 Tm 168.9	552 Yb 173.0	553 Ac 227.0	554 Th 232.0	555 Pa

Name Solutions

If you wish to have your final exam and course grade posted on the Web site, please provide me with a four (4) digit number which will be the ID number for your grade.

Four (4) digit number for posting.

(09) 1. Short Answer (No explanation required)

- (a) True/False: The derivative, $d\psi/dx$, must be continuous at boundaries in which the potential energy is finite (i.e. $V < \infty$).

True

- (b) Is the operator d^2/dx^2 Hermitian?

Yes

- (c) Is the function, $Ae^{-\beta x}$, an Eigenfunction of the $\hat{p}^2$ operator?

Yes

(06) 2. Calculate the commutator: $\left[\frac{d}{dx}, x^2\right]$

$$\left[\frac{d}{dx}, x^2\right]\psi = \frac{d}{dx}(x^2\psi) - x^2 \frac{d\psi}{dx} = \left(\cancel{x^2 \frac{d\psi}{dx}} + \psi \cdot 2x\right) - \cancel{x^2 \frac{d\psi}{dx}}$$

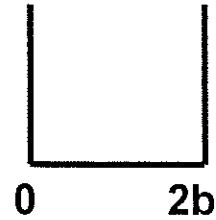
$$= 2x\psi$$

← This is OK too

$$\therefore \left[\frac{d}{dx}, x^2\right] = 2x$$

- (12) 3. Consider a particle in a box, defined by the potential

$$\begin{aligned} V(x) &= 0 & 0 \leq x \leq 2b \\ V(x) &\rightarrow \infty & x < 0, x > 2b \end{aligned}$$



A suitable normalized wavefunction for this particle is: $\psi = A[x^2 - 2bx]$, $A = \sqrt{\frac{15}{16b^3}}$

Calculate the expectation value for the kinetic energy, $\left\langle \frac{p^2}{2m} \right\rangle$,

as a function of $\hbar$, b and m

$$\frac{d\psi}{dx} = A(2x - 2b) \quad \frac{d^2\psi}{dx^2} = 2A$$

$$\left\langle \frac{p^2}{2m} \right\rangle = \int_0^{2b} \psi \left(-\frac{\hbar^2}{2m} \right) \frac{d^2\psi}{dx^2} dx = \int_0^{2b} A(x^2 - 2bx) \left(-\frac{\hbar^2}{2m} \right) (2A) dx$$

$$= -A^2 \frac{\hbar^2}{m} \int_0^{2b} (x^2 - 2bx) dx = -A^2 \frac{\hbar^2}{m} \left[\frac{x^3}{3} - 2b \frac{x^2}{2} \right]_0^{2b}$$

$$= -\frac{A^2 \hbar^2}{m} \left[\frac{(2b)^3}{3} - b(2b)^2 \right] - 0$$

$$= -\frac{A^2 \hbar^2}{m} \left(\frac{8b^3}{3} - 4b^3 \right) = -\frac{A^2 \hbar^2}{m} \left(-\frac{4}{3} b^3 \right)$$

$$\rightarrow \left(\frac{15}{16b^3} \right) \frac{\hbar^2}{m} \left(\frac{4b^3}{3} \right) = \frac{5}{4mb^2} \hbar^2$$

$$= \frac{5}{4mb^2} \frac{\hbar^2}{4\pi^2} = \boxed{0.032 \frac{\hbar^2}{mb^2}}$$

- (15) 4. The first two lines in the rotational Raman spectrum ($\Delta J = +2$) of the linear molecule SiO_2 [$^{16}\text{O} = ^{28}\text{Si} = ^{16}\text{O}$] are found at (1) 0.936 cm^{-1} , and (2) 1.560 cm^{-1} .

- (5) a) Calculate the frequency (in cm^{-1}) of the **fourth (4th.)** line in the rotational Mookster Spectrum of SiO_2 . The selection rule for the Mookster Spectrum is

$$\Delta J = +3$$

$$\bar{\nu}_1 = 6\bar{B} = 0.936 \text{ cm}^{-1} \rightarrow \boxed{\bar{B} = 0.156 \text{ cm}^{-1}} \quad \bar{\nu}_2 = 10\bar{B} = 1.560 \text{ cm}^{-1} \rightarrow \boxed{\bar{B} = 0.156 \text{ cm}^{-1}}$$

Makster's rule: $J=3 \rightarrow J=6$ $\bar{\nu} = \frac{E_6}{hc} - \frac{E_3}{hc} = 6(7)\bar{B} - 3(4)\bar{B}$
 $= 30\bar{B}$

$$\bar{\nu} = 30(0.156) = \boxed{4.68 \text{ cm}^{-1}}$$

- (10) b) Calculate the Si=O bond length, in Å.

$$I = \frac{h}{8\pi^2 Bc} = \frac{6.63 \times 10^{-34}}{8(3.14)^2(0.156)(3 \times 10^8)} = 1.794 \times 10^{-45} \text{ kg m}^2$$

$$I = \sum m_i r_i^2 = M_{\text{O}} r_{\text{SiO}}^2 + m_{\text{Si}}(0)^2 + m_{\text{O}} r_{\text{SiO}}^2 = 2 M_{\text{O}} r_{\text{SiO}}^2$$

$$I = 2 M_{\text{O}} r_{\text{SiO}}^2$$

$$\therefore r_{\text{SiO}}^2 = \frac{I}{2 M_{\text{O}}} = \frac{1.794 \times 10^{-45} \text{ kg m}^2}{2(2.658 \times 10^{-26} \text{ kg})}$$

$$= 3.375 \times 10^{-20} \text{ m}^2$$

$$r_{\text{SiO}} = \sqrt{3.375 \times 10^{-20} \text{ m}^2} = 1.84 \times 10^{-10} \text{ m} \times \frac{1 \text{ Å}}{10^{-10} \text{ m}} = 1.84 \text{ Å}$$

$$(0.184 \text{ nm also OK})$$

$$\text{O} = \text{Si} = \text{O}$$

$$r_{\text{SiO}} / r_{\text{SiO}}$$

$$M_{\text{O}} = 16 \times 10^{-27} \text{ kg} \times \frac{1}{6.02 \times 10^{23} \text{ mol}^{-1}} = 2.658 \times 10^{-26} \text{ kg}$$

(20) 5. The radial portion of one of the wavefunctions of the He^+ ion is:

$$R(r) = re^{\frac{-r}{a_0}}$$

(10) (a) Calculate the **normalized** radial distribution function [RDF(r) = $P(r)$] for an electron with this wavefunction (i.e. calculate the Normalization Constant, B).

Note: Your value for B should be a function of a_0

$$P(r) = B r^2 R^2 = B r^2 (r e^{-r/a_0})^2 = B r^4 e^{-2r/a_0}$$

$$1 = \int_0^\infty P(r) dr = B \int_0^\infty r^4 e^{-2r/a_0} dr = B \int_0^\infty r^4 e^{-\alpha r} dr$$

$\alpha = 2/a_0$

$$1 = B \frac{4!}{\alpha^{4+1}} = B \frac{24}{(2/a_0)^5} = B \frac{24}{32} a_0^5 = B \frac{3a_0^5}{4}$$

$$B = \frac{4}{3a_0^5}$$

#5 Cont'd

(10) (b) The potential energy between the electron and the helium nucleus is given by:

$$V = -\frac{2e^2}{4\pi\epsilon_0 r}$$

Calculate the **average** value of the potential energy between the electron and nucleus.

You should leave your answer in terms of e , $4\pi\epsilon_0$, and a_0 .

$$\begin{aligned} V &= \left\langle -\frac{2e^2}{4\pi\epsilon_0 r} \right\rangle = \frac{-2e^2}{4\pi\epsilon_0} \left\langle \frac{1}{r} \right\rangle = -\frac{2e^2}{4\pi\epsilon_0} \left(\frac{1}{2a_0} \right) \\ &= \boxed{-\frac{e^2}{4\pi\epsilon_0 a_0}} \end{aligned}$$

$$\begin{aligned} \left\langle \frac{1}{r} \right\rangle &= \int_0^\infty P(r) \times \frac{1}{r} dr = \int_0^\infty B r^4 e^{-2r/a_0} \times \frac{1}{r} dr \\ &= B \int_0^\infty r^3 e^{-2r/a_0} dr = B \frac{3!}{(2/a_0)^4} = B \frac{6 a_0^4}{16} \\ &= \left(\frac{4}{3a_0^5} \right) \times \frac{3a_0^4}{8} = \frac{1}{2a_0} \end{aligned}$$

- (8) 6. Consider a particle in a two dimensional box of length $a \times b$, where $b = \frac{a}{\sqrt{2}}$

Draw a table (or diagram) containing the lowest 5 energy levels of a particle in a two dimensional box of dimensions $a \times \frac{a}{\sqrt{2}}$.

Put the energies in units of $\frac{h^2}{ma^2}$ and show the set of quantum numbers corresponding to each level

$$E_{n_x, n_y} = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2}$$

$$= \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8m(\frac{a}{\sqrt{2}})^2}$$

$$= \frac{n_x^2 h^2}{8ma^2} + \frac{2n_y^2 h^2}{8ma^2}$$

$$= \frac{h^2}{ma^2} \left[\frac{n_x^2 + 2n_y^2}{8} \right]$$

n_x	n_y	$E (\frac{h^2}{ma^2})$
1	1	$\frac{3}{8} = 0.38$
2	1	$\frac{6}{8} = 0.75$
1	2	$\frac{9}{8} = 1.13$
3	1	$\frac{11}{8} = 1.38$
2	2	$\frac{12}{8} = 1.50$

- (6) 7. The three experimental ionization energies of the lithium atom are: $IE_1 = 5.39$ eV, $IE_2 = 75.66$ eV, $IE_3 = 122.40$ eV.

The correlation energy of the lithium atom is -0.046 au.

The Hartree-Fock energy of the Lithium +1 ions is: $E_{HF}(Li^+) = -7.236$ au

Use this data to determine the **Hartree-Fock estimate** of the first ionization energy of Li, in eV.

Note: It should be similar in magnitude, but not the same, as the experimental ionization energy (5.39 eV).

$$E_{\text{exact}}(Li) = -\sum IE$$

$$= -[5.39 + 75.66 + 122.40]$$

$$= -203.45 \text{ eV} \times \frac{1 \text{ au}}{27.21 \text{ eV}}$$

$$= -7.477 \text{ au}$$

$$E_{\text{exact}}(Li) = E_{HF}(Li) + E_{\text{corr}}(Li)$$

$$\begin{aligned} \therefore E_{HF}(Li) &= E_{\text{exact}}(Li) - E_{\text{corr}}(Li) \\ &= -7.477 - (-0.046) \\ &= -7.431 \text{ au} \end{aligned}$$

$$I_{\text{HFF}} \approx E_{HF}(Li^+) - E_{HF}(Li)$$

$$= -7.236 - (-7.431)$$

$$= 0.195 \text{ au} \times 27.21 \text{ eV} = 5.31 \text{ eV}$$

- (20) 8. The bonding in Lithium Hydride (LiH) can be described by a two orbital interaction between the $2s$ orbital on Lithium and the $1s$ orbital on Hydrogen. The Hamiltonian matrix elements (and overlap) are:

$$H_{\text{LiLi}} = -8 \text{ eV} \quad H_{\text{HH}} = -14 \text{ eV} \quad H_{\text{LiH}} = -4.0 \text{ eV} \quad S_{\text{LiH}} = 0$$

Assume that the molecular wavefunction is: $\psi = c_{\text{Li}} 2s_{\text{Li}} + c_{\text{H}} 1s_{\text{H}}$

- (8) a) Set up the Secular Determinant and solve for the energy of the Bonding Orbital.

$$\begin{vmatrix} H_{\text{LiLi}} - \langle E \rangle & H_{\text{LiH}} \\ H_{\text{LiH}} & H_{\text{HH}} - \langle E \rangle \end{vmatrix} = 0 = \begin{vmatrix} -8 - \langle E \rangle & -4 \\ -4 & -14 - \langle E \rangle \end{vmatrix}$$

$$(-8 - \langle E \rangle)(-14 - \langle E \rangle) - (-4)(-4) = 0$$

$$112 + 22\langle E \rangle + \langle E \rangle^2 - 16 = 0$$

$$\langle E \rangle^2 + 22\langle E \rangle + 96 = 0$$

$$\begin{aligned} \langle E \rangle &= \frac{-22 \pm \sqrt{(22)^2 - 4(1)(96)}}{2(1)} = \frac{-22 \pm \sqrt{100}}{2} \\ &= \frac{-22 \pm 10}{2} \end{aligned}$$

$$\langle E \rangle_{\text{bond}} = \frac{-22 - 10}{2} = -16.0$$

$$\left(\langle E \rangle_{\text{anti-bond}} = \frac{-22 + 10}{2} = -6.0 \right)$$

8. Cont'd.

- (8) b) Use your answer in part (a) to calculate the **normalized** coefficients, c_H and c_{Li} , in the bonding orbital. Be sure to normalize the orbital.

Note: If you don't like your answer for part (a), assume that $E_{\text{bond}} = -20$ eV (not the right answer) to work this part.

$$(H_{LiLi} - \langle \delta \rangle) c_{Li} + H_{LiH} c_H = 0$$

$$[-8 - (-16)] c_{Li} + -4 c_H = 0$$

$$8 c_{Li} - 4 c_H = 0 \rightarrow c_H = 2 c_{Li}$$

$$\psi = c_{Li}(2s_{Li}) + c_H(1s_H) = c_{Li}[2s_{Li} + 2(2s_H)]$$

$$\because c_{Li}^2(1^2 + 2^2) = 1 \rightarrow c_{Li} = \frac{1}{\sqrt{5}} = 0.447 = 0.45$$

$$\because \psi = 0.45(2s_{Li}) + 0.90(1s_H)$$

- (4) c) Assume for this part that the antibonding orbital is: $\psi = N[0.65 \cdot 2s_{Li} + 0.35 \cdot 1s_H]$

What fraction of the charge of an electron in the antibonding orbital is on the Lithium atom?

$$F_{Li} = \frac{c_{Li}^2}{c_{Li}^2 + c_H^2} = \frac{(0.65)^2}{(0.65)^2 + (0.35)^2} = 0.775$$

≈ 0.78

(18) 9. QM Methods and Basis Sets

(3) (a) In the CISD(T) method, what does each letter stand for?

Configurations Interaction with Single & Double Excitations
+ Terms of Triple Excitations

(3) (b) Consider the 4-31G (aka STO-4-31G) basis set. What does each number stand for?

4 - 1 core STO - Lin comb of 4 GTO's
3 - inner valence STO - Lin comb of 3 GTO's
1 - outer valence STO - single GTO

(9) (c) Consider using the 6-311+G(d,2p) to perform a Quantum Mechanical calculation on the HSF molecule. Describe the types and numbers of STOs that are used on each of the 3 atoms (H, F and S)

H
3(1s) - split

2(3x2p) - 2 sets of p plasma

F
1(1s) core
3(2s) spherical
3x3(2p) "
1x5(3d) Polar
11s - diffuse
3(np) - diffuse

S
1(1s) core
1(2s) core
1x3(2p) core
3x(3s) spherical
3x3(3p) "
5(3d) - polar
11s - diffuse
3(np) - diffuse

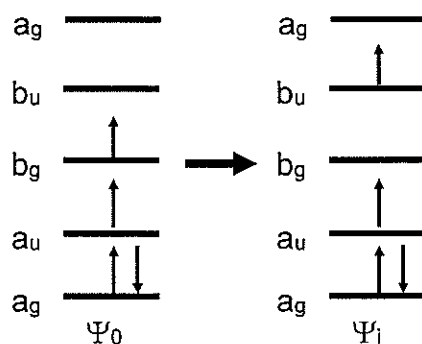
(3) (d) Why is the Hartree-Fock method called a "Self-Consistent" (SCF) method.

Because the solution to the equations is iterated (repeated)
until the calculated field (i.e. the coefficients) stop changing.

- (08) 10. Consider the electronic transition below, arising from the lowest triplet state of (E)-1,2-dichloroethene [C_{2h} symmetry], ... $(a_g)^2(a_u)^1(b_g)^1$ [diagram below and character table in information section at top of exam].

Show whether or not the transition is allowed, **AND**, if it is allowed, is it polarized **parallel** or **perpendicular** to the principal axis.

You MUST show your work to receive credit!!



$$\Gamma(\psi_0) = a_u \times b_g = B_u$$

$$\Gamma(\psi_1) = a_u \times b_u = B_g$$

$$M_x: \Gamma = \Gamma(\psi_1) \Gamma(x) \Gamma(\psi_0)$$

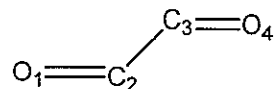
$$= B_g \times B_u \times B_u = B_g \neq A_g$$

$$M_y: \text{Same } \Gamma = B_g \neq A_g$$

$$M_z: \Gamma = B_g \times A_u \times B_u = A_g \checkmark$$

Transition is allowed and polarized parallel to the principal axis.

(18) 11. Consider the molecule, ethanedial (right)



The oxygen Hückel parameters are: $\alpha_o = \alpha + \beta$

$$\beta_o = 0.8\beta$$

Notes: (1) H atoms on C₂ and C₃ are not shown

(2) Each O atom contributes one (1) electron to the π -system

(8) a) Write the Secular Determinant in terms of (i) α , β and E, (ii) $x = (\alpha - E)/\beta$

$$0 = \begin{vmatrix} \alpha - E & \beta_o & 0 & 0 \\ \beta_o & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta_o \\ 0 & 0 & \beta_o & \alpha - E \end{vmatrix} = \begin{vmatrix} \alpha + \beta - E & 0.8\beta & 0 & 0 \\ 0.8\beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & 0.8\beta \\ 0 & 0 & 0.8\beta & \alpha + \beta - E \end{vmatrix}$$

Div. by β to get $x = \frac{\alpha - E}{\beta}$

$$0 = \begin{vmatrix} x + 1 & 0.8 & 0 & 0 \\ 0.8 & x & 1 & 0 \\ 0 & 1 & x & 0.8 \\ 0 & 0 & 0.8 & x + 1 \end{vmatrix}$$

11. Cont'd.

$n_{e^-} = 4$ (each C, O contributes $1e^-$)

For Parts b-d: The two occupied MOs and their energies are:

$$\begin{array}{ll} \phi_1 = 0.50 \chi_1 + 0.50 \chi_2 + 0.50 \chi_3 + 0.50 \chi_4 & E_1 = \alpha + 1.80 \beta \quad \frac{1L}{2L} \\ \phi_2 = 0.67 \chi_1 + 0.23 \chi_2 - 0.23 \chi_3 - 0.67 \chi_4 & E_2 = \alpha + 1.28 \beta \quad \frac{1L}{2L} \end{array}$$

(3) b) Determine the π electron charge on O₁.

$$q_1 = 2(0.5)^2 + 2(0.67)^2 = \boxed{1.40}$$

(3) c) Determine the O₁-C₂ bond order (P_{12}).

$$P_{12} = 2(0.5)(0.5) + 2(0.67)(0.23) = \boxed{0.81}$$

(4) d) The energy of the occupied π orbital in formaldehyde ($H_2C=O$) is $E_1 = \alpha + 1.44\beta$. Calculate the π Delocalization Energy in Ethanal.

$$\begin{aligned} E_{\pi} &= 2(\alpha + 1.80\beta) + 2(\alpha + 1.28\beta) \\ &= 4\alpha + 6.16\beta \end{aligned}$$

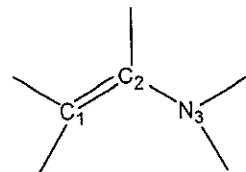
$$E_{loc} = 2[2(\alpha + 1.44\beta)] = 4\alpha + 5.76\beta$$

$$\begin{aligned} E_{deloc} &= E_{\pi} - E_{loc} = [4\alpha + 6.16\beta] - [4\alpha + 5.76\beta] \\ &= \boxed{0.40\beta} \end{aligned}$$

(10) 12. Consider the ethenamine molecule (on right).

The Secular Determinant is:

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 0.8 \\ 0 & 0.8 & x+1.5 \end{vmatrix} = 0 \quad \text{where } x = \frac{\alpha - E}{\beta}$$



The two solutions to the Secular Determinant corresponding to occupied orbitals are $x_1 = -1.95$ and $x_2 = -0.68$.

Determine the **normalized** Anti-bonding Molecular Orbital, ϕ_2 , corresponding to $x_2 = -0.68$ as a linear combination of the basis functions, χ_1 , χ_2 and χ_3 (χ_3 is on the nitrogen).

$$x_1 c_1 + c_2 + 0 c_3 = 0 \rightarrow c_2 = -x_1 c_1 = -(-0.68) c_1 = 0.68 c_1$$

$$\begin{aligned} c_1 + x_2 c_2 + 0.8 c_3 &= 0 \rightarrow c_3 = \frac{-x_2 c_2 - c_1}{0.8} = \frac{-(-0.68)(0.68 c_1) - c_1}{0.8} \\ &= \frac{0.462 c_1 - c_1}{0.8} = -0.672 c_1 \approx -0.67 c_1 \end{aligned}$$

$$\begin{aligned} \phi_2 &= c_1 \chi_1 + c_2 \chi_2 + c_3 \chi_3 \\ &= c_1 [\chi_1 + 0.68 \chi_2 - 0.67 \chi_3] \end{aligned}$$

$$c_1^2 [1^2 + (0.68)^2 + (-0.67)^2] = 1 \rightarrow c_1 = \frac{1}{\sqrt{1.913}} = 0.72$$

$$\begin{aligned} \phi_2 &= 0.72 [\chi_1 + 0.68 \chi_2 - 0.67 \chi_3] \\ &= 0.72 \chi_1 + 0.49 \chi_2 - 0.48 \chi_3 \end{aligned}$$