UNIVERSITI
TEKNOLOGI
PETRONAS

FINAL EXAMINATION
MAY 2024 SEMESTER

COURSE	:	**YBB4024 - QUANTUM AND COMPUTATIONAL CHEMISTRY**
DATE	:	**5 AUGUST 2024 (MONDAY)**
TIME	:	**2:30 PM - 5:30 PM (3 HOURS)**

INSTRUCTIONS TO CANDIDATES

1. Answer **ALL** questions in the Answer Booklet.
2. Begin **EACH** answer on a new page in the Answer Booklet.
3. Indicate clearly answers that are cancelled, if any.
4. Where applicable, show clearly steps taken in arriving at the solutions and indicate **ALL** assumptions, if any.
5. **DO NOT** open this Question Booklet until instructed.

Note :

i. There are **TEN (10)** pages in this Question Booklet including the cover page and appendices.

ii. **DOUBLE-SIDED** Question Booklet.

1. a. Calculate the uncertainty in the position of an electron given the uncertainty in its velocity is 2×10^{-3} cm s^{-1}.

[4 marks]

b. The work function for metallic cesium is 2.14 eV. Determine the kinetic energy and the speed of the electrons emitted when illuminated by light with a wavelength of 300 nm.

[4 marks]

c. Calculate the probability of finding a particle in between 0.45 *L* and 0.47 *L* in a box of length *L* for the following quantum numbers.

i. 3d

[4 marks]

ii. 6f

[4 marks]

d. For a harmonic oscillator with an effective mass of 3.07×10^{-25} kg, the energy difference between adjacent levels is 4.55×10^{-21} J. Determine the force constant of the oscillator.

[4 marks]

2. a. If the number of J = 3 ← 2, the rotational transition of $^{1}H^{35}Cl$ considered as a rigid rotor is 63.56 cm^{-1}, calculate the moment of inertia and bond length of the molecule.

[5 marks]

b. Determine the angular momentum and the number of nodes (both angular and radial) for an electron in the 5f and 4d orbitals.

[4 marks]

c. Calculate the zero-point energy of a harmonic oscillator consisting of a particle with mass of 5.16×10^{-26} kg and force constant of 285 N m^{-1}.

[2 marks]

d. Determine whether the following atomic transitions are dipole-allowed in the normal electronic emission spectrum of an atom.

i. $5d \rightarrow 2s$

[2 marks]

ii. $5p \rightarrow 3s$

[2 marks]

e. The molar absorption coefficient of a solute at 440 nm is 300 $dm^3\ mol^{-1}\ cm^{-1}$. When light of this wavelength passes through a 5.50 mm cell containing a solution of the solute, 64.0% of the light is absorbed. Calculate the concentration of the solution.

[5 marks]

3. a. The compound $CH_3CH=CHCHO$ has a strong absorption in the ultraviolet at 46,950 cm^{-1} and a weak absorption at 30,000 cm^{-1}. Justify these features in terms of the structure of the molecule.

[5 marks]

b. Suppose that an atom has six electrons in the outer orbitals. Determine the possible values of the total spin quantum number, S using Clebsch-Gordon series and its multiplicity.

[3 marks]

c. Determine the ground state energy for an electron that is confined to a box which is 0.55 nm wide.

[2 marks]

d. Calculations based on fundamental principles, such as *ab initio* methods, are prioritized over those that incorporate some experimental data (semi-empirical calculations). Justify your response.

[3 marks]

e. Explain the main factor responsible for the differences in geometries or relative energies obtained using electronic structure calculation techniques like *ab initio* or DFT, compared to those derived from molecular mechanics.

[3 marks]

f. The time step (∂t) is a critical parameter governing the frequency at which the positions and velocities of simulated particles (atoms or molecules) are updated during a simulation. Discuss the factors that need to be considered when determining the appropriate ∂t.

[4 marks]

4. a. The bond-bending energy of a water molecule, with an angle of 130.6°, is 4.00 kcal mol^{-1}. Given a bending force constant (k_{bend}) of 50 kcal mol^{-1} $radian^{-2}$, calculate the equilibrium bond angle (θ_{eq}) (1° = 0.017 radians).

[4 marks]

b. Calculate the electrostatic attraction between the Na^+ and Cl^- ions if the distance between the two is 5 Å. ($\varepsilon_0 = 8.854 \times 10^{-12}$ F m^{-1})

[4 marks]

c. There are two popular minimization algorithms (first order method) used to optimize geometry of molecules. These algorithms evaluate the force that acts on the coordinate to drive the equation towards finding lower energy coordinates.

i. Choose **ONE (1)** algorithm and explain how the chosen algorithm work.

[5 marks]

ii. Design a 3D quadratic function and use the chosen algorithm in **part (c)(i)** to predict the **FIVE (5)** coordinates given the initial coordinates of (4, 4, 2). Propose one suitable time step to be used and justify your selection.

[5 marks]

iii. Sketch the Potential Energy Surface (PES) showing the decrease of energy with respect to the coordinates based on the solution provided in **part (c)(ii).**

[2 marks]

5. a. A molecular dynamics simulation is performed on a roughly spherical protein with a diameter of 40 Å. Periodic boundary conditions are applied using a cubic box, where the side length L is chosen such that the protein, when centered in the box, is at least 20 Å away from each edge. Calculate the number of water molecules required to fill the remaining space in the box, assuming each water molecule occupies 29.9 $Å^3$.

[5 marks]

b. Solve Newton's equation of motion with the Verlet integrator to obtain the final Velocity Verlet algorithms for a new position, $q(t + \delta t)$ and a new velocity, $v(t + \delta t)$.

[7 marks]

c. Explain the stages involved in the Velocity Verlet algorithm for updating the positions and velocities of particles.

[4 marks]

d. When using periodic boundary conditions, every atom present in the simulation box, with coordinates (x, y, z), is accompanied by an infinite number of periodic images with coordinates ($x+n_xL_x$, $y+n_yL_y$, $z+n_zL_z$), where the n's are integers, and L_x, L_y and L_z are the lengths of the box in each direction. Consider a cubic box (L = 30 Å in each direction) and two atoms A and B with (x_A, y_A, z_A) = (29, 14, 28) and (x_B, y_B, z_B) = (2, 15, 1), calculate the distance between the two closest images of A and B.

[4 marks]

-END OF PAPER-

APPENDIX 1

LIST OF FORMULA

$$\Psi = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right)$$

$$p = mv$$

$$\hbar = \frac{h}{2\pi}$$

$$\Delta p \Delta x \geq \frac{1}{2}\hbar$$

$$E_K = h\nu - \phi$$

$$E_K = \frac{1}{2}mv^2$$

$$\lambda = \frac{h}{p}$$

$$E_{photon} = \frac{hc}{\lambda_{photon}}$$

$$E = (V + \frac{1}{2})\hbar\omega$$

$$\omega = \sqrt{\frac{k_f}{m}}$$

$$\Delta E_v = E_{v+1} - E_v = \hbar\omega$$

$$I_{II} = 2m_H R^2(1 - cos\theta)$$

$$E = \frac{l(l+1)\hbar^2}{2I}$$

$$I = m_{eff}R^2$$

$$r = \mathrm{R}\sin\theta$$

$$I = \sum mr^2$$

$$E_J = B_o J(J+1)$$

$$I = \frac{\hbar J}{2\pi c v}$$

selection rule, $\Delta l = \pm 1$

$$Radial\ nodes = n - l - 1$$

$$< L >^{\frac{1}{2}} = \hbar\sqrt{l(l+1)}$$

$$J = \hbar\sqrt{l(l+1)}$$

$$j = 1 \pm \frac{1}{2}$$

$$E = -\frac{hcZ^2R_H}{n^2}$$

$$E = \frac{h^2n^2}{8mL^2}$$

$$Bond\ order = \frac{1}{2}(n - n^*)$$

$$B = \frac{\hbar}{4\pi cI}$$

$$\bar{\nu} = 2BJ$$

$$\nu = 2\bar{B}c(J+1)$$

$$I_{11} = 2m_H R^2(1 - \cos\theta)$$

$$\Delta\bar{\nu} = 2\bar{B}(J+1) - 2\bar{B}J$$

$$\Delta\bar{\nu} = 2\bar{B}$$

$$I = \mu R^2$$

$$G(v) = \left(v + \frac{1}{2}\right)\bar{\nu}$$

$$\Delta G(v) = \left(v + \frac{1}{2}\right)\bar{\nu} - \left(v + \frac{1}{2}\right)^2 x_e\bar{\nu}$$

$$log\frac{I_0}{I} = \varepsilon[J]l = A$$

$$m_{eff} = \mu = \frac{m_1m_2}{m_1 + m_2}$$

$$Multiplicity = 2S + 1$$

$$E_{elec} = \sum \frac{q_iq_ie^2}{4\pi\varepsilon_0 r_{ij}}$$

$$sphere\ volume, V = \frac{4}{3}\pi R^3$$

APPENDIX 2

PHYSICAL CONSTANTS

Atomic mass unit	1 amu	=	1.661×10^{-24} g
	1 g	=	6.022×10^{23} amu
Avogadro's number	N	=	6.022×10^{23} / mol
Boltzmann's constant	k	=	1.381×10^{-23} J/K
Electron charge	e	=	1.602×10^{-19} C
Faraday's constant	$F = Ne$	=	9.649×10^{4} C/mol
Gas constant	R	=	8.314 J/mol-K
		=	0.08206 L-atm/mol-K
Mass of electron	m_e	=	9.110×10^{-31} kg
Mass of neutron	m_n	=	1.675×10^{-27} kg
Mass of proton	m_p	=	1.673×10^{-27} kg
Atomic mass constant	m_u	=	1.660×10^{-27} kg
Pi	π	=	3.142
Planck's constant	h	=	6.626×10^{-34} Js
	$\hbar$	=	1.055×10^{-34} Js
Speed of light	c	=	2.998×10^{8} m/s
Rydberg constant	R_H	=	1.097×10^{7} m^{-1}
	hcR_H	=	2.179×10^{-18} J

APPENDIX 3

CONVERSION FACTORS AND FORMULAS

Length: SI unit: meter (m)	**Pressure: SI unit : Pascal (Pa)**
1 km = 0.62137 mi	1 Pa = 1 N m^{-2}
1 mi = 5280 ft	= 1 kg $m^{-1}s^{-2}$
= 1.6093 km	1 atm = 101325 Pa
1 m = 1.0936 yd	= 760 torr
1 in. = 2.54 cm	= 760 mmHg
1 cm = 0.39370 in.	= 14.70 lb in^{-2} (or psi)
1 Å = 10^{-10} m	1 bar = 10^5 Pa
	= 750 torr
	= 750 mmHg
Mass: SI unit: kilogram (kg)	**Volume: SI unit: cubic meter (m^3)**
1 kg = 2.2046 lb	1 L = 10^{-3} m^3
1 lb = 453.59 g	= 1 dm^3
= 16 oz	= 10^3 cm^3
1 amu = 1.66054 x 10^{-24} g	= 1.0567 qt
	1 gal = 4 qt
	= 3.7854 L
	1 cm^3 = 1 mL
	1 in^3 = 16.39 cm^3
Energy	
1 eV = 1.60218 x 10^{-19} J	

APPENDIX 4

LIST OF ELEMENTS

Name	Symbol	Atomic number	Atomic weight	Name	Symbol	Atomic number	Atomic weight
Actinium	Ac	89	227.03[a]	mendelevium	Md	101	258.10[a]
Aluminium	Al	13	26.98	mercury	Hg	80	200.59
Americium	Am	95	243.06[a]	molybdenum	Mo	42	95.94
Antimony	Sb	51	121.75	neodymium	Nd	60	144.24
Argon	Ar	18	39.95	neon	Ne	10	20.18
arsenic	As	33	74.92	neptunium	Np	93	237.05[a]
astatine	At	85	209.99[a]	nickel	Ni	28	58.69
barium	Ba	56	137.33	niobium	Nb	41	92.91
berkelium	Bk	97	247.07[a]	nitrogen	N	7	14.01
beryllium	Be	4	9.01	nobelium	No	102	259.10[a]
bismuth	Bi	83	208.98	osmium	Os	76	190.23
bohrium	Bh	107	264.12[a]	oxygen	O	8	16.00
boron	B	5	10.81	palladium	Pd	46	106.40
bromine	Br	35	79.90	phosphorus	P	15	30.97
cadmium	Cd	48	112.41	platinum	Pt	78	195.08
calcium	Ca	20	40.08	plutonium	Pu	94	244.06[a]
californium	Cf	98	251.08[a]	polonium	Po	84	208.98[a]
carbon	C	6	12.01	potassium	K	19	39.10
cerium	Ce	58	140.12	praseodymium	Pr	59	140.91
cesium	Cs	55	132.91	promethium	Pm	61	145.00[a]
chlorine	Cl	17	35.45	protactinium	Pa	91	231.04
chromium	Cr	24	52.00	radium	Ra	88	226.03[a]
cobalt	Co	27	58.93	radon	Rn	86	222.02[a]
copper	Cu	29	63.55	rhenium	Re	75	186.21
curium	Cm	96	247.07[a]	rhodium	Rh	45	102.91
dubnium	Db	105	262.11[a]	rubidium	Rb	37	85.47
dysprosium	Dy	66	162.50	ruthenium	Ru	44	101.07
einsteinium	Es	99	252.08[a]	rutherfordium	Rf	104	261.11[a]
erbium	Er	68	167.26	samarium	Sm	62	150.35
europium	Eu	63	151.96	scandium	Sc	21	44.96
fermium	Fm	100	257.10[a]	seaborgium	Sg	106	266.00[a]
fluorine	F	9	19.00	selenium	Se	34	78.96
francium	Fr	87	223.02[a]	silicon	Si	14	28.09
gadolinium	Gd	64	157.25	silver	Ag	47	107.87
gallium	Ga	31	69.72	sodium	Na	11	23.00
germanium	Ge	32	72.61	strontium	Sr	38	87.62
gold	Au	79	196.97	sulfur	S	16	32.07
hafnium	Hf	72	178.49	tantalum	Ta	73	180.95
hassium	Hs	108	269.13[a]	technetium	Tc	43	98.00[a]
helium	He	2	4.00	tellurium	Te	52	127.60
holmium	Ho	67	164.93	terbium	Tb	65	158.93
hydrogen	H	1	1.01	thallium	Tl	81	204.37
indium	In	49	114.82	thorium	Th	90	232.04
iodine	I	53	126.90	thulium	Tm	69	168.93
iridium	Ir	77	192.22	tin	Sn	50	118.71
iron	Fe	26	55.85	titanium	Ti	22	47.90
krypton	Kr	36	83.80	tungsten	W	74	183.84
lanthanum	La	57	138.91	uranium	U	92	238.03
lawrencium	Lr	103	262.11[a]	vanadium	V	23	50.94
lead	Pb	82	207.19	xenon	Xe	54	131.30
lithium	Li	3	6.94	ytterbium	Yb	70	173.04
lutetium	Lu	71	174.97	yttrium	Y	39	88.91
magnesium	Mg	12	24.31	zinc	Zn	30	65.39
manganese	Mn	25	54.94	zirconium	Zr	40	91.22
meitnerium	Mt	109	268.14[a]				