

Key for the Chemical Physics Cumulative Exam

January 21, 2009

There are 40 questions and each is worth 3 points. Be precise and concise.

1. Define an electron volt (eV)

The energy acquired by an electron in falling through a potential drop of 1 Volt

2. What is the unit of energy in the SI system?

Joule

3. What are the units of a quadrupole moment?

Charge(length)²

4. What are the units of Planck's constant?

Energy*time

5. What is the numerical value of kT at room temperature (specify units)?

Approximately 1/40 eV

6. Write an equation for the energy levels of a harmonic oscillator. Define all symbols.

$$E_n = h\nu \left(n + \frac{1}{2} \right)$$

h Planck's constant, ν the vibrational frequency of the harmonic oscillator and n the vibrational quantum number $0, 1, 2, \dots, \infty$

7. Write an equation for the rotational energy levels of a diatomic molecule. Assume rigid rotation and define all symbols.

$$E_j = \frac{\hbar^2}{2I} j(j+1) \text{ where } \hbar = \frac{h}{2\pi}, I \text{ the moment of inertia of the diatomic}$$

and j the rotational quantum number $0, 1, 2, \dots, \infty$

8. How does the energy of a one electron atom depend on the principal quantum number n and the nuclear charge Z ?

$$E \propto -\frac{Z^2}{n^2}$$

9. What is the order of magnitude of a nuclear diameter? (Specify units)

$$10^{-13} \text{ cm}$$

10. How is the electrostatic potential at a point in space related to the electric field at that point?

If \vec{E} is the electric field at \vec{r} and $\phi(\vec{r})$ is the electrostatic potential then
$$\vec{E} = -\nabla\phi$$

11. What is the first Law of Thermodynamics?

The energy of a system and its surroundings is constant.

12. What is the second Law of Thermodynamics?

It is impossible to convert heat into work with 100% efficiency.

13. Define a Hermitian Operator

An operator \hat{O} is Hermitian if it is self adjoint. This insures that
$$\int \psi^* \hat{O}\psi d\tau = \int (\hat{O}\psi)^* \psi d\tau$$

14. Distinguish between Fermions and Bosons.

Fermions have half integer spin while Bosons have integer spin or 0

15. Distinguish between Rayleigh and Raman scattering.

Rayleigh is elastic while Raman scattering is inelastic

16. Distinguish between states and levels.

A state is a solution to the Shrodinger equation
A level is a collection of states with the same energy.

17. What is a normal coordinate?

Normal coordinates are those in which the vibrational potential energy function is diagonal and in the harmonic approximation has the form $\frac{1}{2} \sum_{i=1} Q_i^2$

18. Distinguish between fluorescence and phosphorescence.

Fluorescence is radiation resulting from a transition between two singlet states. Phosphorescence is radiation resulting from the transition between a singlet and triplet state.

19. Distinguish between stationary and non-stationary states.

In a stationary state $\psi^*(\vec{r}, t)\psi(\vec{r}, t) = \psi^*(\vec{r})\psi(\vec{r})$

In a non-stationary state $\psi^*(\vec{r}, t)\psi(\vec{r}, t) \neq \psi^*(\vec{r})\psi(\vec{r})$ and is time dependent.

20. Evaluate the commutator $[\hat{x}, \hat{p}_x]$

Since $[\hat{x}, \hat{p}_x]f(x) = \hat{x}\hat{p}_x f - \hat{p}_x\hat{x}f$ and $\hat{p}_x = \frac{\hbar}{i} \frac{d}{dx}$ we see that

$[\hat{x}, \hat{p}_x]f(x) = i\hbar f(x)$ for arbitrary $f(x)$ and so $[\hat{x}, \hat{p}_x] = i\hbar$

21. What is a Rydberg state?

A state in which an electron is excited to an orbital with a large principal quantum number and is so distant from the nucleus/nuclei and other electrons that the orbital it occupies resembles a hydrogenic orbital.

22. What is the wavelength of a 5 eV photon?

$$\frac{12396(\text{eV} \cdot \text{\AA})}{5(\text{eV})} = 2479 \text{\AA}$$

23. What is the Franck-Condon approximation?

When a molecule absorbs radiation it happens so fast that the nuclei cannot respond immediately so the geometry of the molecule in the excited state is initially that of the ground state.

24. What is meant by pre-dissociation?

When two potential curves cross a molecule can make a transition from the bound states of one curve to the continuum states of the second.

25. What is a Dirac delta function?

If $\delta(x-a)$ is a Dirac delta function then $\int_{-\infty}^{+\infty} \delta(x-a)f(x)dx = f(a)$

26. What is Fermi's Golden Rule?

If a system is subjected to a periodic perturbation of the form $\hat{H}e^{-i\omega t}$ where \hat{H} is time independent then the average transition rate from state ψ_i to state ψ_f is proportional to $\left| \langle \psi_i | \hat{H} | \psi_f \rangle \right|^2 \delta(E_f - E_i - \hbar\omega)$

27. What is the Auger effect?

If one excites two electrons in an atom or molecule to an energy level which is greater than the energy of the atomic or molecular +1 ion and a free electron the system can eject an electron and form the +1 ion.

28. What is the antisymmetrizing operator?

Given a product of one particle functions $\phi_A(1)\phi_B(2)\phi_C(3)\cdots\phi_D(N)$ the antisymmetrizing operator \hat{A} will convert the product into a determinant

$$\hat{A}\phi_A(1)\phi_B(2)\phi_C(3)\cdots\phi_D(N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_A(1) & \phi_A(2) & \cdots & \phi_A(N) \\ \phi_B(1) & \phi_B(2) & \cdots & \phi_B(N) \\ \vdots & \vdots & \vdots & \vdots \\ \phi_D(1) & \phi_D(2) & \cdots & \phi_D(N) \end{vmatrix}$$

29. State the Variation theorem.

Given a Hamiltonian \hat{H} and its associated ground state eigenvalue and eigenfunction $\hat{H}\psi_0 = E_0\psi_0$ and a function ϕ that satisfies the same boundary conditions as E_0 then $\langle \phi | \hat{H} | \phi \rangle \geq E_0$

30. Write down the time dependent Schrodinger equation. Define all symbols.

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

\hat{H} is the hamiltonian and $\Psi = \Psi(\vec{r}, t)$ is the time dependent wavefunction

31. What is the effect of spin-orbit interaction on the 2P state of the H atom?

The spin orbit interaction will couple the orbital angular momentum ($l = 1$) and the spin angular momentum ($s = 1/2$) into to possible total angular momenta $j = 1/2$ & $3/2$ with the $j = 1/2$ level lowest.

32. What is the relation between the frequency of vibration of a diatomic molecule and its force constant?

In the harmonic approximation $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$

Where ν is the frequency, k the force constant and μ the reduced mass.

33. Write down the ideal gas law. Define all symbols.

$PV = nRT$ where P is the pressure, V the volume, R the gas constant, T the temperature and n the number of moles of gas.

34. What is the Maxwell-Boltzmann distribution of kinetic energies?

The fraction of molecules with an energy between E & $E + dE$ is proportional to $\sqrt{E}e^{-\beta E}dE$ where $\beta = 1/kT$ and k is the Boltzmann constant.

35. What does the acronym DFT stand for?

Density Functional Theory

36. What are the SI units of a dipole moment?

Coulomb*Meter

37. What is the dielectric constant of liquid water?

Approximately 80

38. What is a partition function?

$$q = \sum_{i=1}^{states} e^{-E_i/kT} \quad \text{Where } E_i \text{ is the energy of the } i^{th} \text{ state}$$

39. Give an example of a molecule with D_{3h} symmetry.



40. Define the de Broglie wavelength.

$$\lambda = \frac{h}{p} \text{ where } p \text{ is the linear momentum.}$$