The following constants may be used in this test:

Planck's constant: $h = 6.6 \times 10^{-27}$ erg sec
electron mass: $m = 9.1 \times 10^{-28}$ g
$c = 3.0 \times 10^{10}$ cm/sec

DIRECTIONS: Each item in this examination consists of a question or an incomplete statement which is followed by four possible choices. Select the single choice that best answers the question or completes the statement. Then on your answer sheet blacken with your pencil the space between the dotted lines having the same number as your choice.

Sample:

101. Water is composed of
(1) hydrogen and nitrogen.
(2) carbon monoxide and hydrogen.
(3) hydrogen and oxygen.
(4) sulfur and phosphorus.

Sample Answer Sheet:

101. 1::::: 2::::: 3▬ 4:::::

The best answer is hydrogen and oxygen; therefore, answer space 3 has been marked on the sample answer sheet.

SUBTEST III.

QUANTUM CHEMISTRY

PART III A

1. DeBroglie's hypothesis leads to the relationship
(1) $E = mc^2$.
(2) $\lambda = hmv$.
(3) $\lambda = mv/h$.
(4) $\lambda = h/mv$.

2. If the uncertainty in locating the position of an electron is estimated to be 1 Å, the uncertainty in its momentum (erg sec/cm) is approximately
(1) $\frac{h}{4\pi}(1 \times 10^{-8})$
(2) $\frac{h}{4\pi}(1 \times 10^{8})$
(3) zero
(4) $\frac{h^2}{4\pi^2}(1 \times 10^{-8})(3 \times 10^{10})$

3. If the wave function $\Psi = \cos(\alpha x)$ is an eigenfunction of the operator d^2/dx^2, what is the corresponding eigenvalue?
(1) $-\alpha^2$
(2) α^2
(3) $\cos(\alpha x)$
(4) $\cos(\alpha x)$ is not an eigenfunction of d^2/dx^2

4. For a system in which Ψ is an un-normalized real wave function the average value of x^2 is
(1) $\int \Psi x^2 \Psi dV$
(2) $\int \Psi x^2 \Psi dV / \int \Psi\Psi dV$
(3) $\int \Psi^2 x \Psi^2 dV$
(4) $\int \Psi\Psi dV$

5. A photon has an energy of one electron volt, ($1 \text{ ev} = 1.6 \times 10^{-12}$ ergs). The wave length of the photon is
(1) 18.6×10^{-4} cm.
(2) 3660 Å.
(3) 3×10^{-5} cm.
(4) 12,400 Å.

6. The degeneracy of the energy level of a hydrogen atom for which $n = 2$ is
(1) 1-fold.
(2) 2-fold.
(3) 3-fold.
(4) 4-fold.

Go on to the next page.

7. Consider an electron in an atom as a particle in a one dimensional box of width of 3×10^{-8} cm. The energy involved in a transition from $n = 1$ to $n = 2$ is about

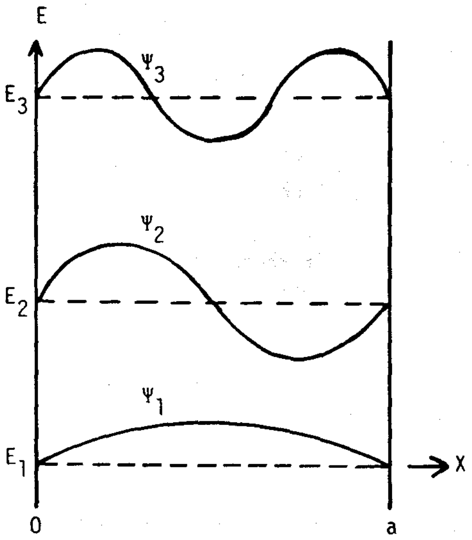
   (1) 2.0×10^{-11} ergs/electron.

   (2) 2.0×10^{-33} ergs/electron.

   (3) 1.0×10^{5} ergs/electron.

   (4) 3 ergs/electron.

8. The solid heavy lines in the figure below represent wave functions for a particle in a box.



   For the particle in the $n = 2$ state when would the particle be found at the exact center; i.e., $x = a/2$, of the "box"?

   (1) Always
   (2) Quite often
   (3) Occasionally
   (4) Never

9. Given the symbols

   k = force constant
   μ = reduced mass
   v = quantum number, 0, 1, 2 . . . .
   ν = frequency

   the quantum energy levels for a one-dimensional harmonic oscillator are given by

   (1) $vh\nu$.

   (2) $(v + 1/2)h\nu$.

   (3) $(v + 1/2)k\mu\nu$.

   (4) $(v - 1/2)h\nu$.

10. The energy levels of a rigid rotor are

   (1) inversely proportional to its moment of inertia.

   (2) directly proportional to its moment of inertia.

   (3) directly proportional to its bond length.

   (4) inversely proportional to the rotational quantum number.

11. The electron spin hypothesis is not required for explanation of

   (1) the anomalous Zeeman effect.

   (2) mass spectra.

   (3) the fine structure splitting of atomic spectra.

   (4) the degeneracy of the excited states of atoms.

12. In a photoelectric cell when electrons are ejected, the number of them ejected per second is

   (1) proportional only to intensity of the incident light.

   (2) proportional only to the frequency of the incident light.

   (3) independent of both frequency and intensity of the incident light.

   (4) dependent on the momentum of the incident light.

13. In applying the variation method of approximation in quantum mechanics, the wave function is adjusted so as to

   (1) make the energy of the system equal to zero.

   (2) maximize the energy of the system.

   (3) minimize the energy of the system.

   (4) make the function an analytical solution of the differential equation in a closed form.

14. In its simplest form, the Schrödinger equation predicts that the energy of the electron in the hydrogen atom

   (1) is a function of $\underline{n}$ only.

   (2) is a function of $\underline{\ell}$ only.

   (3) is a function of $\underline{n}$ and $\underline{\ell}$.

   (4) is a function of $\underline{n}$, $\underline{\ell}$, and $\underline{m}$.

Go on to the next page.

15. The ionization energy of the 1s electron in a He^+ ion is

(1) the same as that of the 1s electron in the hydrogen atom.
(2) twice that of the 1s electron in the hydrogen atom.
(3) one-fourth that of the 1s electron in the hydrogen atom.
(4) four times that of the 1s electron in the hydrogen atom.

16. When an electron is removed from N_2, the N-N bond lengthens; whereas when an electron is removed from O_2, the O-O bond shortens. The most important factor involved in this difference between nitrogen and oxygen is that

(1) oxygen is more electronegative than nitrogen.
(2) the bond distance in neutral nitrogen is longer than in oxygen.
(3) the electron comes from an antibonding MO in oxygen but from a bonding MO in nitrogen.
(4) oxygen has a higher ionization potential than nitrogen.

17. Given the trend in bond angles in the isoelectronic series CH_4, NH_3, H_2O: angle H-C-H = 109.5, angle H-N-H = 107.0, angle H-O-H = 104.5°. The factor primarily responsible for this trend is

(1) the number of lone pairs of electrons.
(2) bond polarity differences.
(3) the central atom ionization potential.
(4) dipole moments.

18. The fact that NF_3 has a smaller dipole moment than does NH_3 is best accounted for by assuming that

(1) the N-F bond is less polar than the N-H bond.
(2) the polar contribution of the lone pair tends to cancel the N-F bond polarity.
(3) both NH_3 and NF_3 molecules are nonplanar pyramidal molecules.
(4) NF_3 has a larger dielectric constant.

19. Crystal field theory predicts that in an octahedral complex such as $[Ni(NH_3)_6]^{2+}$

(1) the degeneracy of the five d orbitals is unchanged from the free Ni^{2+} ion.
(2) the d_{xy}, d_{xz}, and d_{yz} orbitals all increase in energy relative to $d_{x^2-y^2}$ and d_{z^2} orbitals.
(3) the s, p, and d orbitals form a set of dsp^2 hybrid orbitals.
(4) the $d_{x^2-y^2}$ and d_{z^2} orbitals increase in energy relative to the d_{xy}, d_{xz}, and d_{yz} orbitals.

20. The number of vibrational modes or degrees of freedom for the non-linear molecule $SOCl_2$ is

(1) 1	(3) 3
(2) 6	(4) 7

21. At room temperature for which type of internal energy is one likely to find the greatest numbers of molecules occupying states other than the lowest energy state?

(1) Electronic energy
(2) Rotational energy
(3) Vibrational energy
(4) None of these, as a molecule will always be in its ground state at room temperature.

22. N_2 does not show an absorption peak in the infrared region of the spectrum because

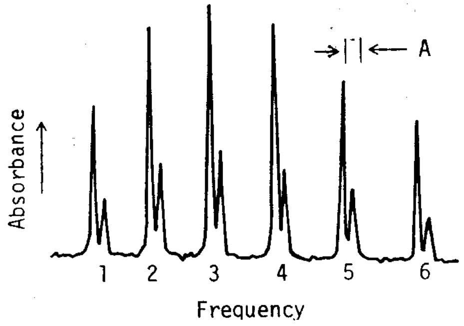
(1) the vibrational energy levels are too widely spaced.
(2) the vibrational energy levels are too close together.
(3) the N_2 molecule does not rotate.
(4) the dipole moment does not change during vibration.

23. Substitution of deuterium for hydrogen in a molecule results in a shift in the infrared absorption frequency of the molecule. This is caused primarily by a change in

(1) electron delocalization.
(2) reduced mass.
(3) force constant.
(4) dipole moment.

Go on to the next page.

24. The diagram shows a portion of the infrared absorption spectrum of HCl.



The splitting A in peak #5 may be attributed to

(1) the difference in masses of the naturally abundant chlorine isotopes, Cl^{35} and Cl^{37}.

(2) the vibrations of the molecule.

(3) the dipole moment of HCl.

(4) the molecular symmetry.

25. The difference between the intensities of peak #3 and peak #6 in the spectrum of HCl shown in question 24 may be attributed to

(1) the dipole moment of HCl.

(2) the population of rotational levels.

(3) the polarizability of HCl.

(4) the quantum mechanical selection rules.

26. In a system composed of n particles behaving classically according to Boltzmann statistics the number of particles which would be found in a state having an energy, ε, and a degeneracy, g, is directly proportional to

(1) ε/h.

(2) $g\varepsilon$.

(3) $ge^{-\varepsilon/kT}$.

(4) $ge^{\varepsilon/kT}$.

27. Which molecule has the most closely spaced rotational levels?

(1) H_2

(2) N_2

(3) O_2

(4) I_2

28. The NMR spectrum of ethanol, CH_3CH_2OH, exhibits three absorption peaks which, at high resolution, are found to be multiplets. For example, the absorption peak due to resonance of the methyl hydrogen atoms consists of a three line multiplet of relative intensities 1:2:1. This results because

(1) there are three possible geometrical conformations of the methylene and hydroxyl hydrogen atoms.

(2) the hydroxyl proton undergoes rapid exchange with water in all but the most highly dried ethanol.

(3) the highly electronegative oxygen atom is shielded from the methyl protons by the methylene protons.

(4) there are four possible spin states of the methylene protons' nuclear spins and two of the states are nearly identical in energy.

29. In the Bragg treatment, the diffraction of X-rays by a crystal is represented as

(1) scattering by electrons.

(2) a Fourier series.

(3) reflection by lattice planes.

(4) absorption by the crystal.

30. In photochemical reactions the quantum yield or efficiency is determined by the number of

(1) energy quanta absorbed by the system.

(2) energy quanta absorbed per reacting molecule.

(3) molecules reacting per energy quantum absorbed.

(4) molecules reacting in the system.

Do *not* continue to Part IIIB unless told to do so.

PART IIIB

31. Which is *not* true for commuting operators A and B?

    (1) $[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0$

    (2) $[\hat{A},\hat{C}] = 0$ if $[\hat{B},\hat{C}] = 0$

    (3) If ϕ_i, ϕ_j are eigenfunctions of $\hat{A}$, then $<\phi_i|\hat{B}|\phi_j> = 0$ unless $i = j$.

    (4) A and B need not have real eigenvalues.

32. Compare an electron in an atom with a helium atom in a box 5.0 cm on an edge treating each case as a particle in a box. When compared to the separations between the allowed energy levels for the electron, the separations between the allowed energy levels for the helium atom are

    (1) much smaller.

    (2) about the same.

    (3) a little greater.

    (4) much greater.

33. According to classical mechanics a harmonic oscillator may be at rest and have zero energy but according to quantum mechanics the lowest energy level is $E = 1/2\ h\nu_0$, called the zero-point energy. This zero-point energy is explained by

    (1) the Heisenberg uncertainty principle.

    (2) the Pauli exclusion principle.

    (3) Hund's rules.

    (4) the Franck-Condon principle.

34. Which wave function for excited electronic states of He does *not* obey the Pauli exclusion principle?

    (1) $[1s(1)2s(2)+2s(1)1s(2)]\ [\alpha(1)\beta(2)-\beta(1)\alpha(2)]$

    (2) $[1s(1)2s(2)-2s(1)1s(2)]\ [\alpha(1)\alpha(2)]$

    (3) $[1s(1)2s(2)+2s(1)1s(2)]\ [\alpha(1)\beta(2)+\beta(1)\alpha(2)]$

    (4) $[1s(1)2s(2)-2s(1)1s(2)]\ [\beta(1)\beta(2)]$

35. The total energy of a molecule can be written, to a good approximation, as the sum of various separate energies:

    $$E_{total} = E_{electronic} + E_{vibrational} + E_{rotational} + E_{translational}.$$

    Which wave function has the proper form to guarantee separation of the energies?

    (1) $\Psi = \frac{1}{4}[\Psi_{el} + \Psi_{vib} + \Psi_{rot} + \Psi_{trans}]$

    (2) $\Psi = \Psi_{el} + \Psi_{vib} + \Psi_{rot} + \Psi_{trans}$

    (3) $\Psi = \Psi_{el}\Psi_{vib}\Psi_{rot}\Psi_{trans}$

    (4) $\Psi = \frac{1}{2}(\Psi_{el} + \Psi_{trans})(\Psi_{vib} + \Psi_{rot})$

36. If Ψ is the wave function of an electron in the hydrogen atom, the probability of finding the electron at a distance between r and r + dr from the nucleus in any direction is given by

    (1) $Ae^{-\Psi/r}$.

    (2) $\frac{\partial^2\Psi}{\partial r^2} + \frac{8\pi^2 m}{r^2}(E - V)\Psi$.

    (3) $4\pi r^2\Psi^2\ dr$.

    (4) $\Psi^2\ dr$.

37. The wave function for H_2 can be written as $\Psi = \phi_{cov} + a\phi_{Ion}$ where ϕ_{cov} represents a wave function for equal sharing of the electrons, ϕ_{Ion} represents complete transfer of the electrons to one H atom, and a is a constant. The method in which a wave function is constructed in this matter is most closely related to the

    (1) uncertainty principle.

    (2) Pauli principle.

    (3) hybridization of atomic orbitals.

    (4) resonance concept.

Go on to the next page.

38. The Born-Oppenheimer approximation is very important when dealing with the Schrödinger equation for a polyatomic molecule. The approximation states that

(1) electronic repulsion may be ignored.

(2) the total energy of the system is conserved.

(3) nuclear and electronic motions may be considered separately.

(4) that the potential and kinetic energy may be separated.

39. A molecule which absorbs radiation in the microwave portion of the spectrum must

(1) have a dipole moment which changes during vibration.

(2) undergo an electronic transition.

(3) have a permanent dipole moment.

(4) undergo a change in polarizability.

40. The fundamental vibrational frequency of HCl is 2886 cm^{-1}, while that of the deuterium compound, DCl, is 2090 cm^{-1}. The reason for the difference in frequencies is that

(1) the HCl force constant is about twice that of DCl.

(2) the DCl reduced mass is about twice that of HCl.

(3) the DCl bond distance is $\sqrt{2}$ that of HCl.

(4) the DCl moment of inertia is $\sqrt{2}$ that of HCl.

41. One can use the Boltzmann distribution statistics for accurate calculations of the thermal energy of physical systems when

(1) there are many more particles than available quantum states.

(2) there are many more available quantum states than particles.

(3) the number of available quantum states and the number of particles are of the same order of magnitude.

(4) the system consists of particles distributed among the available quantum states under conditions of extremely low temperature.

42. Which molecule has C_{3v} symmetry?

(1) H_2

(2) H_2O

(3) NH_3

(4) CO_2

43. The zero-point energy for a mole of a monatomic crystalline solid at 0°K should be (N_A = Avogadro's number)

(1) 0

(2) $(1/2)N_A h\nu$

(3) $N_A h\nu$

(4) $(3/2)N_A h\nu$

44. If the energy level diagram for a hypothetical particle in a system of particles consists of only two levels separated by an energy, ε, the constant volume heat capacity of a mole of these particles

(1) is constant even if temperature changes.

(2) increases continuously with increasing temperature.

(3) increases with temperature to a maximum value.

(4) first increases with temperature to a maximum value, then decreases to zero at high temperatures.

45. In the crystalline form of solid nitrogen known as β-N_2, X-rays indicate that the structure is hexagonal closest packed; this requires the species occupying each lattice point to be spherical. The best explanation for this observation is that

(1) at the low temperature of crystallization the diatomic molecules dissociate into spherical atoms.

(2) Heisenberg's uncertainty principle makes the molecules spherical.

(3) the N_2 molecules are rotating about axes perpendicular to the N-N bond.

(4) N_2 molecules are so small that they appear spherical.

End of test.