CHEMISTRY 163A

PROBLEMS

(6) (a) What is the minimum uncertainty in velocity for an electron in a 1s orbital in a hydrogen atom (assume the electron is confined to a linear region $2a_o$)? If the average velocity of the 1s electron is 2.19×10^6 m s^{-1}, what is the fractional uncertainty?

(b) In parking a 2×10^3 Kg automobile you are moving with an uncertainty in velocity of 0.1 m/sec. What is the uncertainty in position? What fraction of the width of a 10 m parking space is this? Is it likely that you can blame the wave-like properties of matter for the scratch you put on the car when parking?

(7) From the handout on evaluating the Rydberg constant using the correspondence principle:

(a) Briefly, what is the correspondence principle?

(b) Qualitatively, under what conditions (with regard to energy) should $\nu_{qm} = \nu_{cl}$?

(c) Quantitatively, under what limits for ν_{qm} will $\nu_{qm} \rightarrow \nu_{cl}$, i.e., in the correspondence limit how does ν_{qm} depend on R and n?

(8) For the operator $\hat{A} = \frac{+\hbar}{i}\frac{d}{d\phi}$

(a) Which if the following are eigenfunctions:

(i) $\cos m\phi$

(ii) $\sin m\phi$

(iii) $\exp(im\phi)$

(iv) $\exp(-im\phi)$

(b) For any of the examples in (a) which are eigenfunctions what are their respective eigenvalues?

(c) What is $(\hat{A})^2$?

(d) Which of the functions in part (a) are eigenfunctions of $(\hat{A})^2$ and what are their respective eigenvalues?

(9) Find normalization constants for the following functions:

(a) $\sin\left(\frac{2\pi x}{L}\right)$ in (0, L)

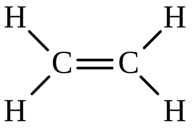
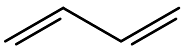
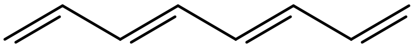
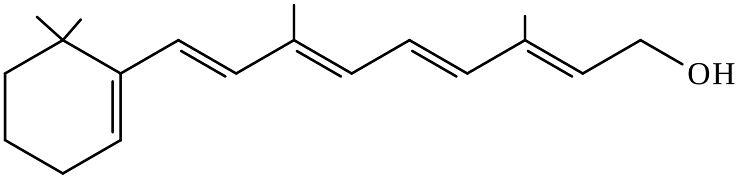
(b) xe^{-x^2} in $(-\infty, \infty)$

(10) McQ. #4-2

*(11) McQ. #3-6

(12) For the n = 2 state of a particle in a one-dimensional box, calculate $\sigma_p = \left(\langle p^2\rangle - \langle p\rangle^2\right)^{1/2}$ [do the calculations of $\langle p\rangle$ and $\langle p^2\rangle$ explicitly, even though the text quotes the results]. Physically interpret the results you obtain for $\langle p\rangle$ and for σ_p.

(13) Approximate energy levels of the π-electrons in conjugated polyenes may be calculated using an electron-in-a-box model. In this approximation the π-electrons are assumed to move in a constant potential in the region of conjugation and to meet an essentially infinite potential barrier at each end of this region. The extent of the region, i.e., the length of the box, can be calculated assuming "single" bond lengths of 1.54×10^{-10} m, "double" bond lengths of 1.35×10^{-10} m, and a distance of 0.77×10^{-10} m, corresponding to a radius of a carbon atom, at *each* end of the polyene. For each of the five molecules:

		$\tilde{\nu}_{obs}$ (cm^{-1})
ethylene		61,728
butadiene		47,619
hexatriene		40,485
octatetrene		34,965
vitamin A		32,680

(a) Calculate L, the length of the box.

(b) What is the energy of the nth π-electron level in such molecules.

(c) Since each "double" bond contributes two electrons to the π-system, a molecule with k double bonds will have the lowest k π-electron levels filled (in its ground state) by pairs of electrons having opposite spins. The lowest energy allowed transition corresponds to the promotion of an electron from the highest energy *occupied* level to the lowest energy *unoccupied* level. For each of the five polyenes calculate the energy of this transition and compare it to the observed energies.

Please summarize results in a table with the following headings:

molecule	no. of π-electrons	L	$\tilde{\nu}_{calc}$ (cm^{-1})	$\tilde{\nu}_{obs}$ (cm^{-1})