

Due Monday, December 14, 2015, Before 5 p.m.

Rules

1. In this exam you can show off your quantum mechanics skills and show what you can do on your own. That means your allowed auxiliaries are:
 - your own notes and your homework, including the posted solution keys;
 - an integral table or an integrator math program such as Mathematica, MatLab, etc., **but only for integrals and numerical matrix work**;
 - a calculator ;
 - a graphics program to plot curves if you think you need to;
 - a list of natural constants (e.g. from your midterm exams);
 - the textbooks for this course.

Do not use the internet (except as mentioned above); do not use any other parts of math programs. Do not talk to anyone except me about this test. Please read and sign the form on the second page and return it with your exam.

2. If you do not understand a problem, you can ask me for clarification. I will be available for your questions at the following times:
 - Wednesday (Dec. 9) 2 p.m. – 4 p.m.;
 - Thursday (Dec. 10): 10 a.m. – noon;
 - Friday (Dec. 11): 9 a.m. – 11 a.m.
 - Monday (Dec. 14): 9 a.m. - 11 a.m. and 1 p.m. – 2 p.m.

I will only talk to one person at a time, not to groups. I will not answer emailed questions, but I will email comments, clarifications, changes, or corrections to everyone if necessary. Please check your email regularly.

3. Write your name clearly onto each page of your answers.
4. Give your result to at least 3 significant digits **in the units specified in the problem**.
5. Make your written answers as clear as possible, so I can follow your reasoning. That also means that the answers should be reasonably organized.

Well-Meant Suggestions

1. The problems do not contain any trick questions or overly messy integrals. If you find that you run into extremely long and complicated expressions, your approach has probably taken you down a wrong path.
2. Check your results for units. Most mistakes in algebra can be caught that way.
3. Read the problems carefully in order to return complete answers.

**You have worked hard and come far this semester, and you learned a lot.
Just show it!**

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Please sign this form and return it with your exam. Thank you!

I hereby affirm that all work in this test is entirely my own. I did not consult with anyone except the instructor, exchange information concerning this exam with anyone else, or use anything other than what is listed as allowed auxiliaries on page 1 of this test. In completing this test I did not violate any of the rules set down on page 1 of this test.

Print Name

Date

Signature

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The Problems

Problem 1:

Consider a particle on a ring with radius R in the xy plane. The particle has mass m and charge q and interacts with an electric field along the x direction with magnitude ε .

- Write down the Hamiltonian of the system as a function of θ . (2 credits)
- Determine the Hamiltonian matrix elements in the basis of particle-on-a-ring eigenkets. (6 credits)
- Set up a matrix to calculate the lowest 10 energy levels, using your favorite math program, with $R = 1$ nm, $\varepsilon = 10^6$ V/cm. Print the matrix and the eigenvalues you get, listing all values (matrix and eigenvalues) **in eV!** (6 credits)

Problem 2:

Let's treat the Morse potential as a function of the displacement x from equilibrium

$$V(x) = D[1 - \exp(-\alpha x)]^2$$

in perturbation theory and see how good this approach is.

- Expand the Morse potential in a power series around $x = 0$ and write it down as a polynomial in x up to quartic terms. (4 credits)
- Write down the Hamiltonian resulting from your treatment in (a) and partition it in an obvious way to use perturbation theory. Write down the zero-order states and energies. (4 credits)
- Use 1st-order perturbation theory to calculate the energies of the lowest three states. (8 credits)
- Evaluate the quality of the 1st-order result compared to the harmonic approximation and the eigenvalues for the Morse oscillator you know (three sentences or less). (4 credits)

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Problem 3:

Bohr's model for the H atom still sees the electron "orbiting" on classical trajectories around the proton, it only restricts the possible radii. How many orbits **per second** will an electron complete in a H atom in quantum state $n = 3$ according to Bohr's model?

(6 credits)

Problem 4:

Consider the H_2^+ molecular ion with the nuclei labeled A and B. The $1s$ orbitals on each atom form the basis for the problem, so that the energy eigenstates $|\psi\rangle$ are given by linear combinations of the atomic orbitals, $|\psi\rangle = a|A\rangle + b|B\rangle$, where $|A\rangle$ represents the electron localized on nucleus A and $|B\rangle$ represents the electron localized on nucleus B (both basis states are normalized). Different from LCAO-MO theory, let's treat $|A\rangle$ and $|B\rangle$ as orthogonal here.

- a.) Write down the Hamiltonian for this problem in matrix form and solve the eigenvalue problem to find the energies of the "bonding" and "anti-bonding" states for the nuclei fixed at some position. Your answer should be in terms of the matrix elements

$$\langle A|\hat{H}|A\rangle = J \text{ and } \langle A|\hat{H}|B\rangle = K . \quad (6 \text{ credits})$$

- b.) Now find the normalized eigenfunctions. Which one is lower in energy, and why (one sentence)?

(6 credits)

Problem 5:

- a.) Zr has the ground state electron configuration $[\text{Ar}](4s)^2(4p)^6(4d)^2(5s)^2$. Determine **all possible complete term symbols and identify the ground state term symbol.**

(4 credits)

- b.) Consider the excited state of the C atom given by the electron configuration $(1s)^2(2s)^2(2p)(3d)$. Write down all possible term symbols belonging to this configuration.

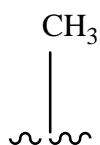
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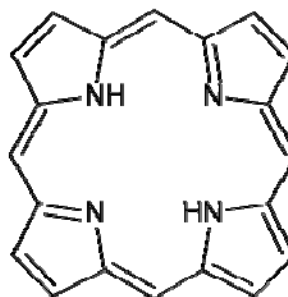
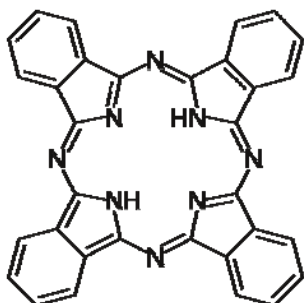
Problem 6:

Consider the physical situations described below and propose a reasonable model to describe each situation (e.g. harmonic oscillator, etc.) out of the models we have touched on this semester. Please name only one model for each problem. Explain your reasoning with one sentence for each model you choose. *(3 credits each)*

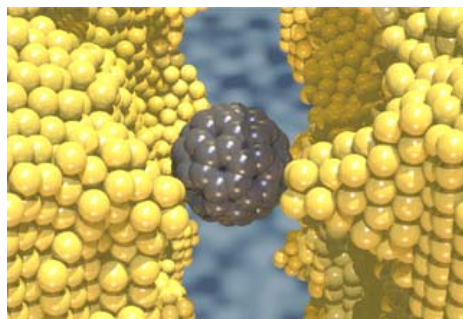
- a.) Model the energy states for the internal rotation of a methyl group anchored on a surface.



- b.) Model the states for electronic motion in the conjugated system of a phthalocyanine (left) or porphyrin (right) molecule.

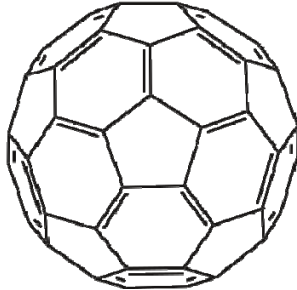


- c.) Model the vibrations of a diatomic molecule.
- d.) Model the mechanical oscillations of a “soccer ball” C₆₀ fullerene molecule trapped between two surfaces.

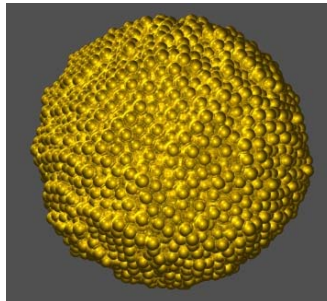


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- e.) Model the motion of an electron in the conjugated system of a “soccer ball” C₆₀ fullerene molecule (all 60 carbon atoms are part of the conjugated system!).



- f.) Model the motion of an electron in a spherical gold nanoparticle (assume that it behaves as a metal would).



Problem 7:

Consider a particle with mass m in a square two-dimensional box. The potential energy function is

$$V(x, y) = \begin{cases} 0 & \text{for } 0 \leq x \leq a \text{ and } 0 \leq y \leq a \\ \infty & \text{everywhere else} \end{cases}.$$

The eigenfunctions for this system are

$$\psi_{n,k}(x, y) = \frac{2}{a} \sin\left(\frac{n\pi x}{a}\right) \sin\left(\frac{k\pi y}{a}\right),$$

where n and k are positive integers.

- Write down the Hamiltonian for the system. *(4 credits)*
- Determine the energy eigenvalues for the system. *(6 credits)*
- Determine the degeneracies g for the lowest 6 states. *(4 credits)*
- Determine the standard deviation of the momentum if the system is in an eigenstate.

Note that the integrals in this part can be a bit lengthy. *(6 credits)*

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Problem 8:

- a.) Qualitatively draw and label the MO diagram of F_2 . (3 credits)
- b.) Qualitatively draw and label the MO diagram of BC. (3 credits)
- c.) Qualitatively draw and label the MO diagram of LiF. The atomic valence energies of Li and F are shown in the table below. (4 credits)

Orbital	Energy in Li [eV]	Energy in F [eV]
2s	-5.3	-42.9
2p		-19.7

Problem 9:

Can position \vec{r} and angular momentum $\vec{\ell}$ of an electron in a 3-dimensional system be measured simultaneously to infinite accuracy? (6 credits)

Problem 10:

Prove that the average value of the number operator \hat{N} in the harmonic oscillator can never be negative for any wave function. (6 credits)

Problem 11:

The quantum mechanical version of the virial theorem can be written as $\langle \vec{r} \cdot \vec{\nabla} V \rangle = 2 \langle \hat{T} \rangle$.

Express the system energy E in terms of $\langle \hat{T} \rangle$ for the one-dimensional quartic oscillator.

(6 credits)

Problem 12:

Prove that $\hat{S}_y |\alpha\rangle = \frac{\hbar i}{2} |\beta\rangle$.

(6 credits)

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Problem 13:

- a.) One can show that for the Morse oscillator, the average potential energy in state v is given by $\langle V_v \rangle = \frac{\hbar\omega_0}{2} \left(v + \frac{1}{2} \right)$. Write down the average value of the kinetic energy in state v . *(2 credits)*
- b.) The vibrational transition $v = 1 \leftarrow 0$ in H_2 has an energy of 4401.21 cm^{-1} . What is the frequency of the corresponding transition in HD, if you approximate the molecule as a harmonic oscillator (**in cm^{-1}**)? *(4 credits)*

Problem 14 – A Few Short Questions (you do not need to justify your answer):

(1 credit each)

- a.) What is the probability of finding an electron in a H atom at $r = 0$ (**the result must be a number**)?
- b.) In the absence of external fields and spin-orbit interaction, is the energy of the H atom in the $3p$ state different than in the $3d$ state (**yes/no**)?
- c.) **True or false:** Any linear combination of two degenerate eigenfunctions of an operator is also an eigenfunction of the operator.
- d.) Will the resolution of an electron microscope become **better or worse** with increasing kinetic energy of the electrons?
- e.) **Complete the following statement with an equation:** A one-dimensional wave function $\psi(x)$ is normalized if ...
- f.) What are the quantum defects for the states of the Deuterium atom? **Your answer must be a number or numbers.**
- g.) **How many** fine structure components does the transition between the $4s^2S$ and the $4p^2P$ terms in atomic potassium contain?
- h.) Does the probability density in the vibrational state $v = 2$ in a Morse oscillator oscillate as a function of time (**yes/no**)?
- i.) Does the term “fine structure” describe the splitting of spectral lines due to external fields (**yes/no**)?
- j.) How many nodal planes in total does the $(\pi_g^* 2p)$ orbital in O_2 have (**the result must be a number**)?

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- k.) How many independent spin functions does atomic nitrogen in its ground state electron configuration (not term!) have (**the result must be a number**)?
- l.) How precisely can you measure the velocity of a proton (**in m/s**) flying in x -direction, if you have determined its x -coordinate to within 2 nm?
- m.) What are the SI units (if any) for the wave function of an electron in a H-atom?
- n.) What is the relative standard deviation, $\Delta E/E$, of the system energy in an eigenstate of the system (**the result must be a number**)?
- o.) What is the commutator equation that describes the fact that $\frac{d\langle \vec{\ell} \rangle}{dt} = 0$ in the H-atom?
- p.) Consider a particle in a harmonic oscillator at a reasonably high quantum number, $v=20$ or so. Is the deBroglie wavelength in the center of the potential **longer or shorter** than close to the edge?
- q.) What is the eigenvalue of the electron spin function $\hat{S}_+|\beta\rangle$ with respect to the z -projection operator of spin in units of \hbar (**the result must be a number**)?
- r.) What is the level of degeneracy of the atomic term 3P_2 in the absence of external fields (**the result must be a number**)?