Quantum Chemistry and Spectroscopy
Exam 1
Oct. 22, 2003

Exams will be collected at 10:20:00 am sharp
Open Book and Open Notes

-ALL ANSWERS MUST BE CIRCLED
-CROSSED OUT/PARTIALLY ERASED WORK WILL BE IGNORED
-NO PARTIAL CREDIT ON NUMERICAL PROBLEMS WITHOUT A FORMULA

Your name:____

Student ID#:____

Signature:____

Total Points: 100

Question 1:__________/10

Question 2:__________/15

Question 3:__________/25

Question 4:__________/32

Question 5:__________/10

Question 6:__________/8

Total: ______________/100

Useful Information:

Workfunctions of Metals:

Li	2.3 eV
Ca	2.87 eV
Al	4.28 eV
Au	5.1 eV

(10 points)

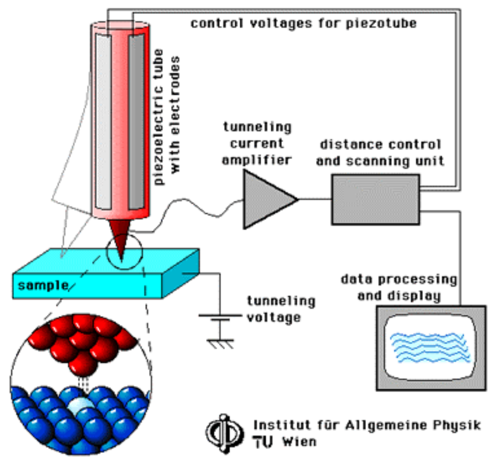
1a) Ultraviolet light with a wavelength of 200 nm is incident upon a clean gold surface in a vacuum chamber. What is the wavelength of the most energetic electrons that are ejected from the surface?

1b) A photomultiplier tube detects photons by amplifying the current generated by the photoelectric effect. Which metal, lithium, calcium, aluminum or gold would you choose if you were trying to make a photomultiplier tube sensitive to the largest portion of the visible spectrum?

(15 Points)

We discussed in lecture that one practical use of quantum mechanical tunneling was in the operation of a scanning tunneling microscope (STM), which can be used to image individual atoms. A schematic of an STM is shown below. A very sharp tip is moved across a conducting surface. If a voltage is applied between the tip and the surface, electrons can tunnel between the two even when they are not in physical contact.

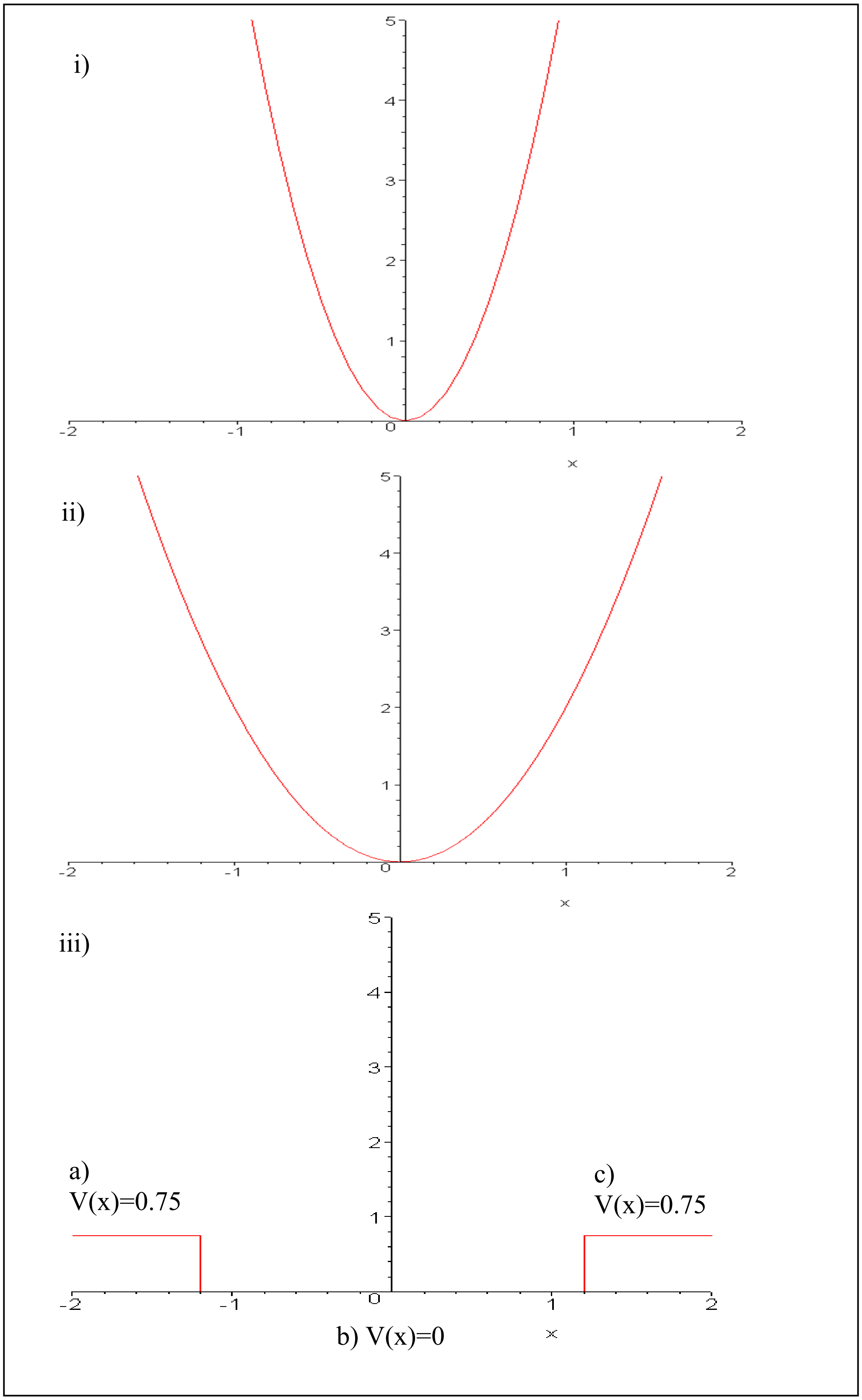
a) Explain qualitatively why we expect the STM to be sensitive to very small changes in the tip-surface distance.



b) Provide a quantitative calculation to back up your answer to part a). Assume that for typical metals and bias voltages the difference between the electron energy E and the barrier height V is approximately 4.5 eV. If the tunneling current is 1 nanoamp when the tip is suspended 0.5 nm above the surface, how much current will pass between the tip and surface if the tip is scanned over bump on the surface the size of an atom (i.e. if the distance were reduced from 0.5 nm to 0.4 nm)

(25 Points)

3) An electron is placed into each of the following 1-D potential wells (i.e. the y-value represents the potential as a function of position along the x-axis):



3-continued
3) An electron is placed into each of the 1-D potential wells on the previous page, the axes labels are in arbitrary units, but are the same scale for each graph. You may assume all lines continue to infinity in their present functional shapes.

3a) In which potential will the electron have the smallest zero point energy? Explain/interpret your answer.

3b) In which potential will the electron have the fewest bound state wavefunctions? (if it not possible to determine with the information provided then explain why not). Explain.

3c) In which potential is the probability of finding the electron at x=0 going to be the highest? How would you calculate the probability of finding the particle between x=0 and x=+infinity (write down an integral calling the wave function ψ). What would the answer be for this potential (you shouldn't need to perform a calculation)?

3d) Write down the time-independent Schrödinger equation for potential *(iii)* and the functional form of the solutions to the time-independent Schrödinger equation for potential *(iii)* in each of the regions *(a), (b)* and *(c)*

3e) What four conditions must you impose on a wave function to obtain a physically valid solution to the Schrödinger equation? Explain how you would use these conditions to obtain the undetermined coefficients in d) (you need not calculate complicated derivatives, but you must explain what needs to be done)

(32 points)
4) A particle is placed in a potential of the form:

$$V(x) = \tfrac{1}{2}bx^2$$

in a state where the wave function of the particle, ϕ, can is given by the equation:

$$\phi = \psi_0 + 2(\psi_2) + \psi_4 + 3(\psi_6)$$

(Here ψ_n represents the n^th^ (normalized) energy eigenfunction of the Hamiltonian with $V(x) = \tfrac{1}{2}bx^2$)

a) True or False: This wavefunction is a linear combination of orthogonal functions. Explain.

b) Is this combination of energy eigenfunctions an eigenfunction of the Hamiltonian operator?

c) If the wave function ϕ is not a solution to the time-independent Schrödinger equation then write out the full time-dependent wave function that includes *t* explicitly assuming the state is in ϕ at t=0.

4d) Is this wavefunction normalized? If not, normalize it. Please write the final solution in terms of the ψ_n

4e) If many systems were prepared in states identical to ϕ and their energies were measured, what would the results of the measurements look like? Discuss both the average value of the results as well as the specific statistical distribution of results (if this is impossible to determine, explain why). If possible, draw a histogram explaining the expected outcome of the measurement, label all axes and key values on any diagrams or graphs.

4f) Does this wave function ϕ have even/odd symmetry? If so, it is even or odd?

(10 Points)

5) A particle is in the state: $\psi = e^{-idx}$ where d is a constant.

a) Is this state an eigenfunction of the momentum operator, p_x? (prove your answer)

b) What is the physical interpretation of this state?

c) What can you say about the position of this particle?

(8 Points) These are questions from the P-chem section of old GRE exams: (CIRCLE THE CORRECT ANSWER)
6)

The presence of a weak band in the infrared absorption spectrum of HCl gas at a frequency roughly twice that of the strong fundamental band can be ascribed to:
a) the presence of different isotopes of chlorine in HCl
b) transitions from the n=1 to the n=2 vibrational state
c) transitions from the n=0 to the n=2 vibrational state
d) changes in electronic energy
e) changes in rotational energy

The energy of which of the following systems is NOT quantized:
a) a particle in a box
b) a particle in free space
c) electrons in the hydrogen atom
d) a simple harmonic oscillator
e) a particle on a ring

In comparison with HCl, the frequency for the transition of DCl from the ground vibrational state to the first excited vibrational state is:
a) higher for DCl
b) lower for DCl
c) sometimes higher and sometimes lower for DCl depending on the temperature and concentration
d) the same for both DCl and HCl
e) not determinable

Which of the following wave number corresponds to energy in the infrared region of the electromagnetic spectrum?
a) 1,700,000 cm^{-1}
a) 100,000 cm^{-1}
a) 33,000 cm^{-1}
a) 20,000 cm^{-1}
a) 2,000 cm^{-1}