

### Worksheet 3. Spectroscopy, Mostly.

1. Some physicists speculate that Planck's constant might not really be constant but, instead, vary slightly in space. A physicist speculates that Planck's constant on the moon is slightly smaller than Planck's constant on earth. We decide to test this hypothesis using the one-dimensional particle in a box. Which of the following observations are would support this hypothesis.

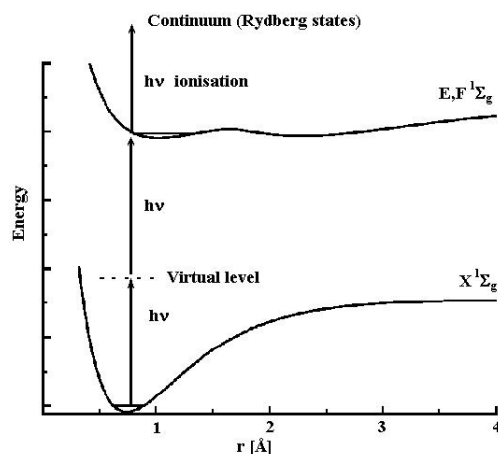
- (a) the zero-point energy of the "moon box" is less than that of the "earth box."
- (b) the zero-point energy of the "moon box" is equal to that of the "earth box."
- (c) the zero-point energy of the "moon box" is greater than that of the "earth box."
- (d) the average position of the particle is further from the edges of the "moon box" than the "earth box."
- (d) the average position of the particle is closer to the edges of the "moon box" than the "earth box."
- (e) the average position of the particle in the "moon box" than the "earth box" is the same.

2. Write down the time-dependent Schrodinger equation.

3. Which of the following common spectroscopic techniques requires going beyond the "weak-field" approximation. (I.e., which of the following experiments requires, at least, second-order time-dependent perturbation theory.)

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|----------------------------|--|------------------------|
| (a) infrared spectroscopy  | (d) X-ray spectroscopy                             | (f) NMR spectroscopy   |
| (b) microwave spectroscopy | (e) ESR/EPR (electron spin resonance) spectroscopy | (g) Raman spectroscopy |
| (c) UV-Vis spectroscopy    |  |                        |

4. The following diagram typifies REMPI (Resonance Enhanced Multiphoton PhotoIonization).



Which of our fundamental approximations is ALWAYS violated in this type of spectroscopy:

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|------------------------------------|------------------------------|
| (a) long-wavelength approximation. | (c) long-time approximation. |
| (b) weak-field approximation.      |                              |

5. Is the lowest excitation energy in the Hydrogen atom ( $1s$  to  $2s$  or  $2p$ ) electric-dipole allowed or forbidden? Explain.
  
6. Is the lowest excitation energy in the Hydrogen molecule ( $H_2$ ;  $\sigma$  to  $\sigma^*$ ) electric-dipole allowed or forbidden? Explain.
  
7. What is the lowest dipole-allowed excitation energy for a particle of mass  $9.1 \times 10^{-31}$  kg in a one-dimensional box of size  $1.2 \times 10^{-10}$  m.
  
8. What is the wavelength of the light that is required to perform the transition in Question 7. Is the long-wavelength approximation likely to be valid here?
  
9. Suppose that the one-dimensional box in Question 7 is oriented along the  $z$  axis. A laser is positioned perpendicular to the box along the  $x$  axis. In order to maximize the number of transitions we observe, we should choose the laser's polarization so that (there may be more than one answer)
 

<ol style="list-style-type: none"> <li>(a) the light is linearly polarized, with the electric field in the <math>y</math> direction.</li> <li>(b) the light is linearly polarized, with the electric field in the <math>z</math> direction.</li> <li>(c) the light is linearly polarized, with the electric field halfway between the <math>y</math> and <math>z</math> directions.</li> <li>(d) the light is linearly polarized, with the magnetic field in the <math>y</math> direction.</li> </ol>	<ol style="list-style-type: none"> <li>(e) the light is linearly polarized, with the magnetic field in the <math>z</math> direction.</li> <li>(f) the light is linearly polarized, with the magnetic field halfway between the <math>y</math> and <math>z</math> directions</li> <li>(g) the light is right-circularly polarized.</li> <li>(h) the light is left-circularly polarized.</li> </ol>
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10. Look in your notes for the expression for electric-quadrupole transitions. Explain why the transition from the  $3d$  metal-based orbital to the  $4s$  metal-based orbital in a weakly coordinated transition metal complex is electric dipole forbidden, but electric quadrupole allowed.