

Questions and Exercises on Quantum Mechanics

Molecular Modeling of Nanosystems – CNE Master

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1. The output of a quantum chemistry calculation for the excited states of a molecule is the following.

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Excited State 1:      Singlet-A      3.9661 eV  312.61 nm  f=0.0008  <S**2>=0.000
 44 -> 49      0.48421
 44 -> 53      0.16656
 48 -> 49      0.45653
 48 -> 53      0.14306

Excited State 5:      Singlet-A      5.3101 eV  233.49 nm  f=0.0143  <S**2>=0.000
 44 -> 49     -0.13288
 44 -> 52      0.11442
 45 -> 50     -0.11475
 45 -> 51      0.24448
 46 -> 50     -0.26164
 47 -> 49      0.50829
 48 -> 49      0.12104
 48 -> 52     -0.19407

Excited State 6:      Singlet-A      5.3517 eV  231.67 nm  f=0.0365  <S**2>=0.000
 44 -> 50      0.13327
 45 -> 49      0.43711
 46 -> 49      0.28620
 46 -> 52     -0.23065
 47 -> 50     -0.12128
 47 -> 51      0.25270
 48 -> 50     -0.24286
```

Based on these data, complete the following table.

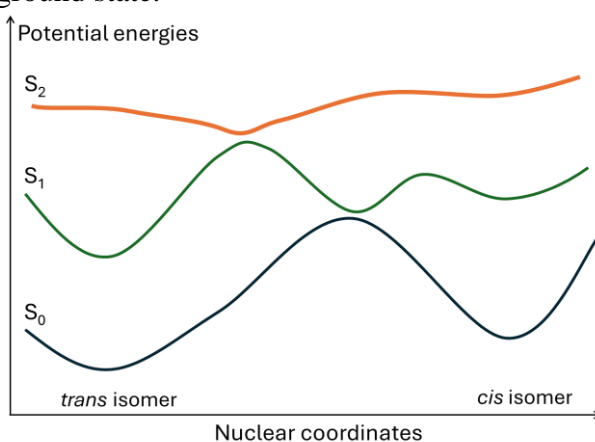
Excited State	Energy (eV)	Oscillator strength	Main orbital transition
1			
2			
3			

2. The table below summarizes the energies of the ground singlet state (S_0) and the first excited singlet state (S_1) of a molecule for different nuclear conformations (S_0 minimum, S_1 minimum, and S_0/S_1 intersection). It also shows the oscillator strength between S_0 and S_1 . Based on these data

- Draw an energy diagram indicating the energy levels as a function of the nuclear geometry.
- What are the absorption and fluorescence energies?
- Explain what may happen to this molecule after it is photoexcited.

Geometry	State	Energy (eV)	Oscillator strength
S_0 minimum	S_0	0.00	-
	S_1	3.10	0.2
S_1 minimum	S_0	0.30	-
	S_1	2.50	0.2
S_1/S_0 intersection	S_0	2.70	-
	S_1	2.70	-

3. A molecular system in the *trans* configuration is photoexcited into the second excited singlet state. The schematic potential energy profile for this system connecting the *trans* and *cis* isomers is illustrated below. Based on this figure, describe the possible deactivation pathways of the system until it relaxes back to the ground state.



4. A photoexcited molecular system can get rid of the energy excess from the light absorption via radiative or nonradiative processes.

- What is the difference between them?
- What are the time scales for each one occurs?
- What is a conical intersection, and how does it relate to the relaxation process?

5. In the time-independent Born-Huang approximation, the nuclear wavefunction χ_n of state n is given by

$$\left(\hat{T}_{nuc} + E_n - \varepsilon\right)\chi_n + \sum_m \hat{N}_{nm}\chi_m = 0$$

where \hat{T}_{nuc} is the nuclear kinetic energy operator, E_n is the electronic potential energy of state n , ε is the molecular energy, \hat{N}_{nm} is the nonadiabatic coupling operator between states n and m , and the summation runs over all states m .

- What is the role of \hat{N}_{nm} in this equation?
- How can the adiabatic (Born-Oppenheimer) approximation be obtained from this equation?
- Write the equation to determine χ_n in the Born-Oppenheimer approximation.

6. The Born-Oppenheimer molecular wavefunction is

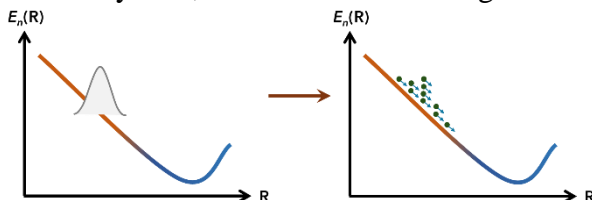
$$\Psi_{BO}(\mathbf{r}, \mathbf{R}) = \chi(\mathbf{R})\phi(\mathbf{r}; \mathbf{R})$$

where \mathbf{r} represents the electronic coordinates, \mathbf{R} represents nuclear coordinates, χ is the nuclear wavefunction, and ϕ is the electronic wavefunction.

- What is the rationale behind this approximation? Why can the nuclear and electronic parts be written as a product?
- What does the semicolon separating \mathbf{r} and \mathbf{R} mean in the electronic wavefunction?
- Born and Huang proposed a more general molecular wavefunction guess. Write it.
- Why is the Born-Huang wavefunction a better approximation than the Born-Oppenheimer wavefunction?

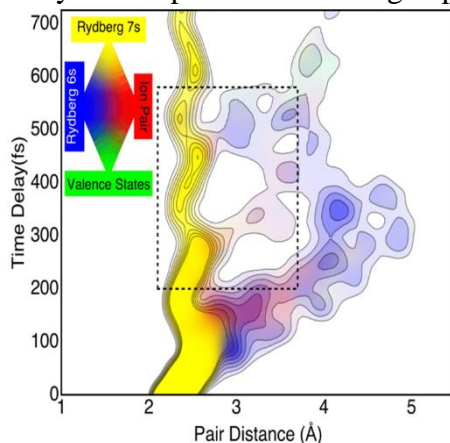
7. Consider the exact molecular wavefunction $\Psi(\mathbf{r}, \mathbf{R})$ or electronic coordinates \mathbf{r} and nuclear coordinates \mathbf{R} . What is the simplified wavefunction format that Born and Oppenheimer proposed to simplify $\Psi(\mathbf{r}, \mathbf{R})$?

8. Under which condition can a nuclear wavepacket be approximated for an ensemble of independent classical copies of the system, as illustrated in the figure?



9. The figure below shows a nuclear wavepacket simulation for CF_3I reported by Yang et al. [*Science*, **2018**, 361, 6397]. The pair distance represents the C-I distance.

- A time zero, what are the most probable C-I distances?
- If we make multiple measurements at 600 fs, which C-I distance should we observe? Which is the most likely?
- Based on this figure, how do you interpret the branching happening around 200 fs?



10. What is quantum decoherence? [This video may help: youtu.be/igsuIuI_HAQ]

11. Sometimes, we represent a quantum state by the state vector $|\psi\rangle$ and others by the wavefunction $\psi(x)$. What are the differences and the relations between these two concepts?

12. For a quantum particle with two possible states (*up* and *down*), a possible basis to describe the quantum state is composed of the kets $|up\rangle$ and $|down\rangle$.

- What is the dimension of this system's Hilbert space?
- If the system contains two of such particles, write a possible basis of kets to describe it. What is the dimension of the Hilbert space?

13. Consider the state $|\Phi\rangle = \frac{1}{\sqrt{2}}(|\psi_1\rangle + |\psi_2\rangle)$

Give the probability of occurrence of output ψ_1 in an experiment, supposing that $|\psi_1\rangle$ and $|\psi_2\rangle$ form an orthonormal basis.