



# Computational Spectroscopy

## II. *ab initio* Methods

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from part (d) Electronic Spectra  
Chemistry 713

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# The Born-Oppenheimer Approximation

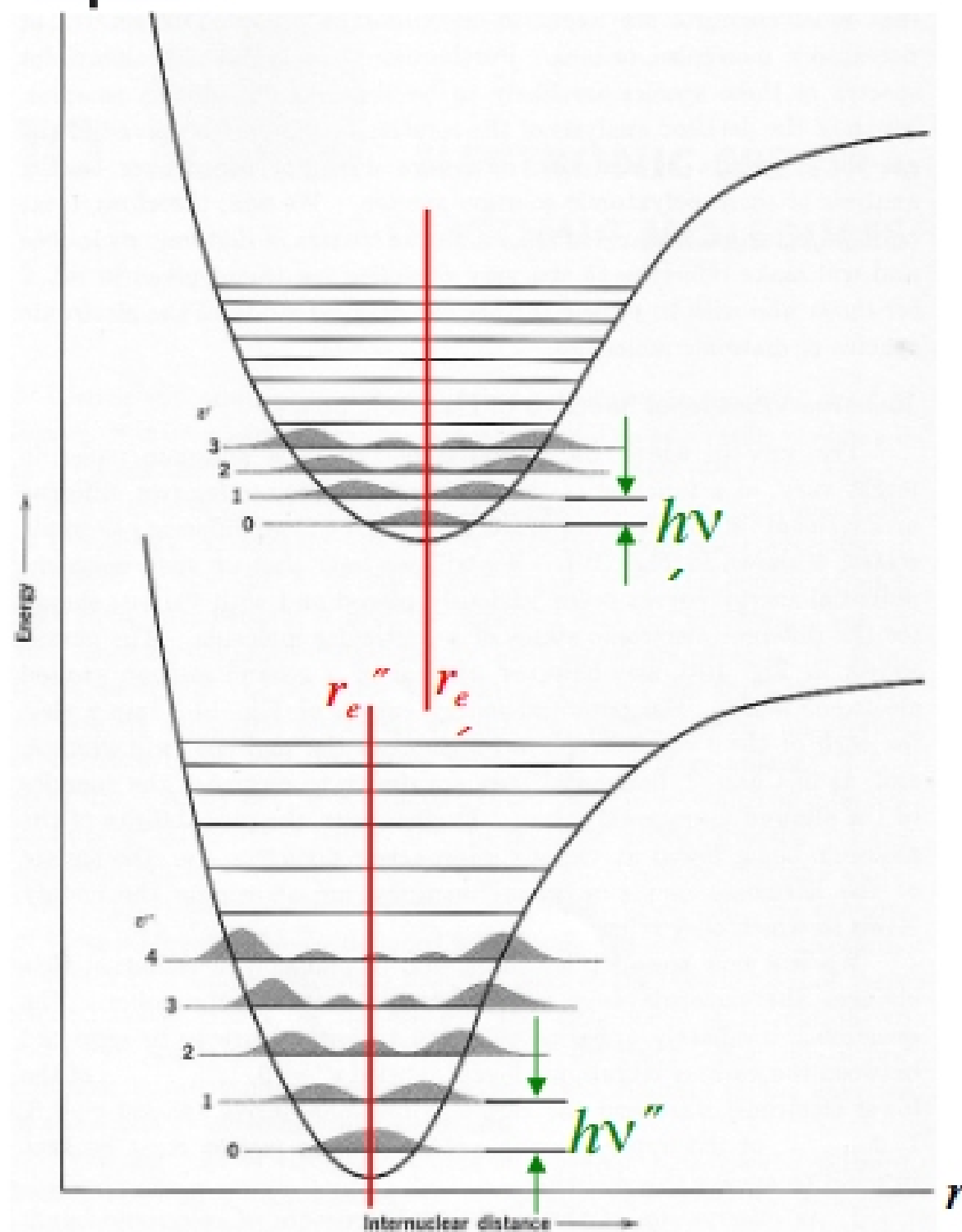
- For a given molecular geometry (i.e., fixed nuclear coordinates,  $\mathbf{R}$ ), solve the electronic Schroedinger equation:

$$H_e \psi_{e,n}(\mathbf{r};\mathbf{R}) = E_n(\mathbf{R})\psi_{e,n}(\mathbf{r};\mathbf{R})$$

where  $H_e$  is the whole molecular Hamiltonian except the nuclear kinetic energy and  $\mathbf{r}$  represents the coordinates for all of the electrons, and  $\psi_e$  is the electronic wave function. Repeat for a range of molecular geometries  $\mathbf{R}$  of interest to construct a potential energy surface.

- The electronic energy  $E_n(\mathbf{R})$  is the potential energy in which the nuclei move.
- Up to now we have just been concerned about the lowest energy electronic state,  $n=0$ .
- To deal with electronic (UV/vis) spectroscopy, we also need to know some of the higher electronic surfaces ( $n=1, 2, \dots$ ) as well.
- The nuclear motion on each surface can then be solved as a separate step.

# The Franck-Condon Principle



- In a diatomic molecule, the potential energy curves are different for lower and upper electronic states.
  - The bond length  $r_e$  changes
  - The vibrational frequency  $\nu$  changes.
- Use double prime for lower state ( $v''$ ), and single primes for upper state ( $v'$ ).