

Preparation for the Final Chem. 474B 2007

Thursday April 25, 2007 2:00 - 5:00 pm Social Sciences Centre Rm. 3102

- 1.) The exam is cumulative; that is, it will cover the entire course. More emphasis however, will be placed on material since the midterm.
- 2.) Relevant formulae will be provided, but as before, it certainly wouldn't hurt to know them off by heart. You must of course understand them.
- 3.) The exam will be a mix of problem solving and descriptive questions. There will be no emphasis on derivations. Problems will be similar to the problem set but clearly in some cases, the amount of detail will be less.
- 4.) Topics covered *since* the midterm include:
Angular momentum (orbital, spin, general) and properties, including eigenvalues, commutator relationships; raising and lowering operators, etc. Selection rules for electric dipole transitions with spin, spin-orbit coupling, Clebsch-Gordon coefficients, H-atom in a Zeeman (magnetic) field (strong and weak field limit), multielectron atomic systems including term symbols, spin-orbit coupling, Hund's rules, Slater determinants, Coulomb and Exchange effects, electron shielding, Hartree-Fock Self Consistent Field Theory, variational theory, periodic table trends, Born-Oppenheimer approximation, solution of the Schrödinger wave equation for the internal motions (vibrations/rotations) of a diatomic molecule, potential energy curves, etc.
- 5.) Study your lecture notes and problem set solutions. I am available for help in my office.

GOOD LUCK!

Differences in the definition of the Electronic Hamiltonian

Sometimes, people define the electronic Hamiltonian within the Born-Oppenheimer approximation as only the kinetic and potential energy of the electrons. i.e. such that it does not include the nuclear-nuclear repulsion energy.

$$\hat{H}^{el} = -\sum_{i=1}^{n_e} \frac{\hbar^2}{2m_e} \nabla(i)^2 - \sum_{I=1}^{N_N} \sum_{i=1}^{n_e} \frac{Z_I e^2}{r_{iI}} + \sum_{i=1}^{n_e-1} \sum_{j=i+1}^{n_e} \frac{e^2}{r_{ij}}$$

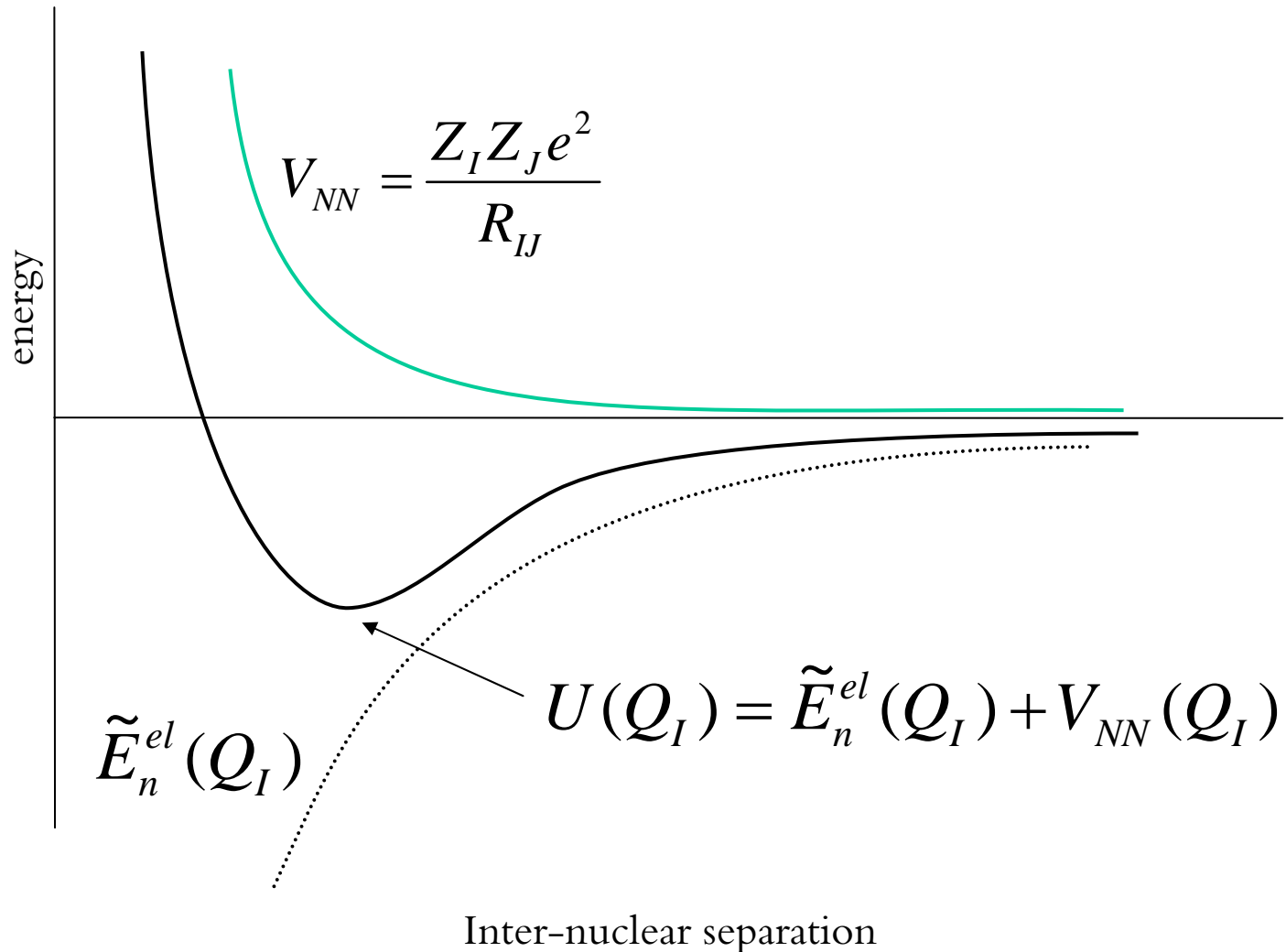
In many ways, this makes sense.

Thus, to switch from one definition to the other, we simply have to add the nuclear-nuclear repulsion energy.

$$E_n^{el}(Q_I) = \tilde{E}_n^{el}(Q_I) + \sum_{I=1}^{N_N-1} \sum_{J=I+1}^{N_N} \frac{Z_I Z_J e^2}{R_{IJ}} = U(Q_I)$$

The potential energy surface is similarly defined.

$$U(Q_I) = \tilde{E}_n^{el}(Q_I) + \sum_{I=1}^{N_N-1} \sum_{J=I+1}^{N_N} \frac{Z_I Z_J e^2}{R_{IJ}}$$



Born-Oppenheimer Approximation - Summary

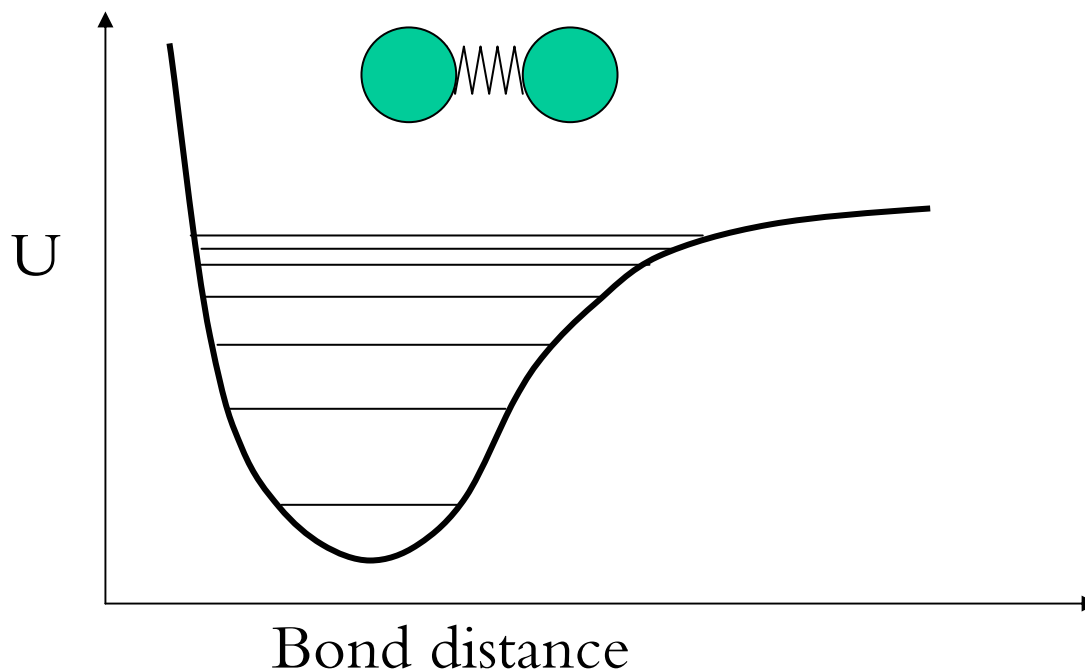
The Born-Oppenheimer approximation is the separation of the motion of the electrons in a molecule from the motion of the nuclei. One practical consequence of the approximation is that the electronic wave function can be calculated for any specific static nuclear framework.

The approximation is based on the great difference in masses between electrons and nuclei.

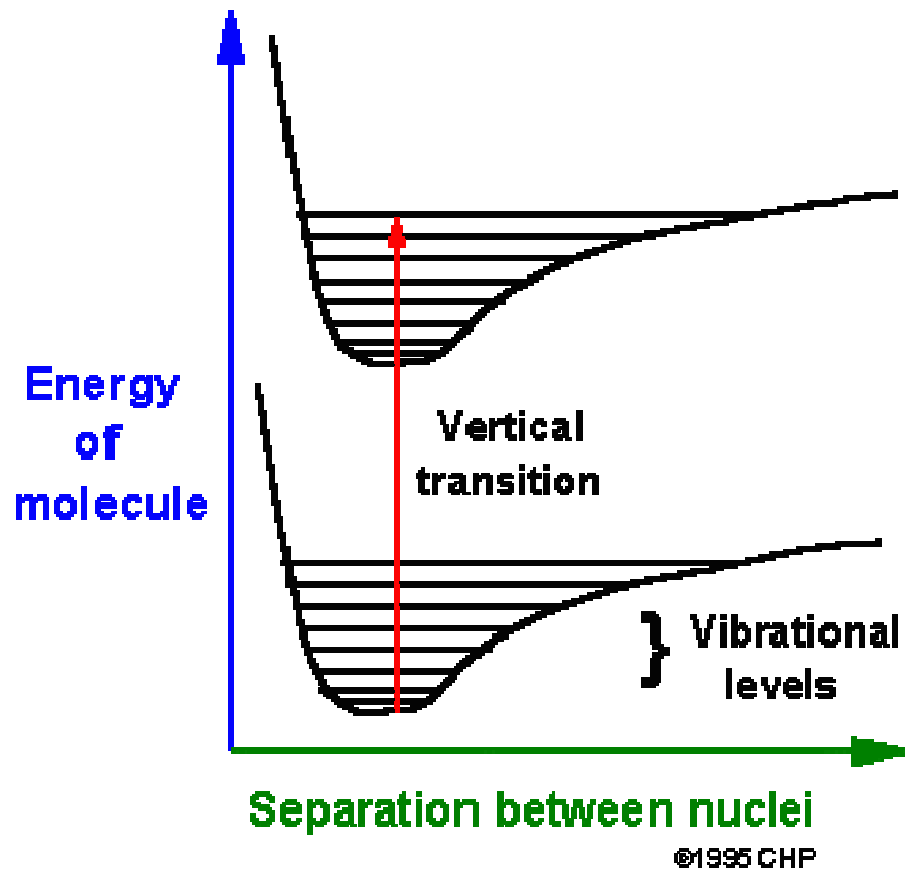
The BO approximation makes it possible to discuss the shape of a molecule in terms of its molecular potential energy surface - for each of its electronic states.

In general the BO approximation is a very good approximation.

The application of the Born-Oppenheimer approximation also allows us to solve for the Nuclear Schrodinger equation, once we have the potential energy surface from our electronic Schrodinger equation.



Quantized energy levels can be solved for from the quantum mechanical harmonic (C374a) or anharmonic oscillator problem, rigid rotor (C374a), non-rigid rotor, etc.



Note: electrons undergo transitions between two potential energy curves much faster than any nuclear motion (vibration or rotation). Thus, transitions are drawn as **vertical**. Non-vertical transitions are unphysical!