**Supplement 9: Chemistry 6854**

**Physical Chemistry Alfred State College**

**A Deeper Look at the Variational Principle of Quantum Approximations**

**(see also: eq.7.3 and 7.4 p. 242 and pp. 241-252)**

The variational principle is in a qualitative sense, self evident. Since the exact wave function solution ψ of any quantum system produces the minimum (correct) energy, any other less perfect solution, call it φ, should produce a higher than minimum energy, e.g. a solution less good than the perfect one.

However, it is possible to incorrectly pick a φ which does not in fact conform to the physical limitation of the system, so that a false minimum less than the correct energy will result.

If is to be a wave function approximating the exact one, ψ, for any quantum mechanical system described by the general energy operator, then φ must therefore abide by the following properties:

a)continuous

b)differentiable

c) normalizable

d satisfies the boundary conditions of the system

Given these properties, then:

**1 Eφ = <φ\*| > Eo (see also: eq.7.3 and 7.4 p. 242)**

This can be proven mathematically as outlined below: (see also, problem 7.1 page 261)

The basic idea is that we can always write the approximate wave function φ as a linear combination of the exact wave function basis set ψ1,ψ2…. So:

 /

Thus:

 Only when n=k will Hkn not = 0 so

 *Eφ = < Σck\* ψko\*|Σcn ψno> = < Σck\* ψko\*Σcn ψno> = Σcn\*cn <ψn| ψn> = Σcn\*cnEno*

*< Σcn ψno|Σcn ψno>< Σcn ψno|Σcn ψno> Σcn\*cn Σcn\*cn*

The denominator is simplified because <ψm|ψn> = δmn (Kronecker delta=> orthogonal)

The numerator term <ψn| ψn> =En since ψn is the exact wave function for solving the eigen value problem and making <ψn| ψn> =En

*Subtracting Eo from Eφ*

*Eφ - Eo = Σcn\*cn (Eno-Eo)*

*Σcn\*cn*

*Since En>o >E­o, the difference (Eno-Eo) > 0 for all n > 0. Moreover, cn\*cn is positive and real for all n so the term on the righ hand side is necessarily >0.*

Thus, anything we do that minimizes Eφ will always produce a value > the exact E for the system.