**Supplement 8: Chemistry 6854**

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 **Variational and Peturbation Approximation Methods: Overview of `Practical’ Quantum Methods (see also: Chapter 7 pp 241-260 of text)**

**8.1. Variational Method (pp 241-251 of text)**

The basic variational principle is that any arbitrary function φ that satisfies the conditions necessary for a wave function (continuity , differentiability, normalizability and obedience to boundary conditions of studied system) will yield a solution energy Eφ such that:

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

If φ = ψo, where ψo is the actual exact solution to the eigen value problem, then φand Eo is the actual energy. Otherwise, Eφ > Eo. The implication of the above is that the closer computed Eφ is to Eo, the better approximation φ is to ψo. Thus, if we can adjust φ to minimize Eφ, then we have a way to approximate ψ using `conveniently’ selected (and simple) φ . This provides a way to model complex quantum systems with `adjusted’ simple `trial’ wave functions φ that reduce the difficulty of solving the exact Schrodinger equation. (`Proof’ of the variational principle is found by working problem 7-1 pg 261 of text.)

It is common to start with one of two kinds of functions:

 i) trial φ which are solutions to a previous and exactly determined Schrodinger eigen value equation e.g. φ = H atom wave functions or harmonic oscillator wave functions,

 ii) φ that are mathematically convenient like cos (kx) , e-ar or

Given one of these two choices, two alternative strategies can then be applied:

1. A `constant’ term in the trial φ can be assigned as a variable (call it β) and Eφ is minimized with respect to β, e.g.

**2** d**Eφ = d [ <φ\*| / ] =0** (see example 7.1 p. 244-5)

 **dβdβ**

This is the most intuitive approach and can be expanded to several variables (α,β, δ….) for minimization.

1. A set of n trial functions of fixed functionality (no adjustable variables (α,β, δ….) are used to approximate ψ as below:

  **n**

 **ψ ≈ c1φ1 +c2φ2 + c3φ3 …cnφn = Σckφk**

 **k=1**

By minimizing the corresponding approximate energy Eφ below with respect to the mixing coefficients c1,c2…cn we eventually are afforded n solutions for Eφ and, by substitution, the individual values for c1,c2,c3…cn.

**3a** Eφ= <Σck\*φk\*|Σ**ck**φ**k> =** <Σck\*φk\*|Σ**ck**φ**k>**

 <Σck\*φk\*|Σckφk> Σckcm<φk\* |φm>

The broad outlines of how this done is explained below.

If we substitute the symbol Hkm =<φk\* |φm> and Skm = <φk\* |φm> and E= Eφ then **3a** becomes **3b**:

**3b** E Σ ckcm Skm = ΣckcmHkm

The expression in **3b** is then separately differentiated with respect to ck for k=1,2…n . A typical result for ck=1 is:

 E(2c1S11 + 2ΣcmSm≠1) + dE(Σ ckcm Skm) = 2c1H11 + 2Σcm≠1H1m

 dc1

Since we are minimizing Eφ => dEφ/dc1 = 0 the above equation simplifies to:

 E(c1S11 + ΣcmS1 m≠1) = c1H11 + Σcm≠1H1m

Rearranging this and expanding the sum we get for k=1:

 c1(H11-ES11) + c2(H12-ES12) + c3(H13-ES13) + …..cn(H1n - ES1n) = 0

Similarly for k= 2,3….n

c1(H21-ES21) + c2(H22-ES22) + c3(H23-ES23) + …..cn(H2n – ES2n) = 0

c1(H31-ES31) + c2(H32-ES22) + c3(H33-ES33) + …..cn(H3n – ES3n) = 0

 …….

c1(Hn1-ESn1) + c2(Hn2-ESn2) + c3(Hn3-ESn3) + …..cn(Hnn – ESnn) = 0

This leads to the general `secular’ equation (determinant), **4:**

**4** Det H11-ES11 H12-ES12 …..H1n -ES1n =0

 H21-ES21 H22-ES22….H2n -ES2n

 …

 Hn1-ESn1 Hn2-En2Sn2.... Hnn-ESnn

The above equation forms the basis of molecular orbital theory, where E is determined by computing the solution of the above once all the Hkm and Skm have been computed and plugged in (usually by computer since it is clearly a tedious business.) Most modern quantum calculations follow this approach. Text books mostly confine themselves to 2 variable (c1 and c2) cases. (See page 250-2 of text, for example. A limited two variable version of the above general solution is also part of problem 7-17 of text, page 263. )

Note that if φk are selected so that Skm = 0 if k≠m, and all Skk = 1 (e.g. φk is orthonormal.) Then **4** simplifies to **5:**

**5** Det H11-E H12 ….H1N =0

 H21 H22-E ….H2N

 …

 Hn1 Hn2  …. HNN

This can be expanded as an nth order polynomial equation in E which can be solved numerically for the n possible E using Maple or other algebraic tricks.

A famous use of **5** is used to derive the orbitals of benzene, a process leading to the 4n+2 Hückel rule.

**8.2. Perturbation Method (pp 257-260 of text)**

In this approach, a well-known system with exactly known wave functions is modified by assuming a small `perturbation’ in the original quantum Hamiltonian is added. For example, if the original energy for the harmonic oscillator is:

o ψo = ( -ħ 2 d2 ψo +½ kx2) ψo = Eoψo

 2μ dx2

then a slight `anharmonicity’ perturbation term like , which accounts for minor deformations in the `spring’ as it stretches out, changes the eigen value problem to:

o + )(ψo + Δψ)= (Eo+ΔE’) )(ψo + Δψ)

Using the proof described in problem 7-19, page 265-266 of text the expansion of the above results in the key recipe **6**:

**6** **ΔE’ = <ψo\*|ψo>**

This means if you can identify or define any perturbation to a known system with known ψo, then to `first order’ the energy of the perturbed system is:

**7 E =Eo +** <ψo\*|ψo>.

For example, if we include anharmonicity in the harmonic oscillator problem, the `corrected’ Ecorr is:

Ecorr = hυ(n+ ½ ) + <ψo\*|ψo>.

Given that ψo = (α/π)1/4  where α=(kμ/ ħ 2 )1/2

* ∞

<ψo\*|ψo>= (α/π)1/4  ∫ dx + (α/π)1/4  ∫ dx

 = 0 +

**E corr(n=0) =** ½ hυ + where α=(kμ/ ħ 2 )1/2  and b is a measure of deformation.

It is this approach that ultimately leads to the fitting equation listed below that was used in the HCl IR experiment . The equation corrects for anharmonicity xe, centrifugal distortion De and rotational-vibrational interaction αe. The observed r2 for the fitted data was better than 0.99999, a testament to the approach.

**Perturbation corrected line position for HCl IR P and R branch rotational lines**

(cm-1) = o +(2Be -2αe)m –αem2 - 4Dem3

where o = e -2exe