

# Approximation Methods

## CHEM 361B: Introduction to Physical Chemistry

Dr. Michael Groves

Department of Chemistry and Biochemistry  
California State University, Fullerton

### Lecture 14

# Table of contents

## 1 Secular Determinants

## 2 Variational Principle

Learning Objective: To apply the variational principle to determine the ground state energy of quantum systems using trial wavefunctions

References:

- McQuarrie Math Chapter F and §8.1 - §8.3

# Solving Systems of Equations

Consider a series of equations that share a common set of variables (say  $x$  and  $y$ ):

$$a_{11}x + a_{12}y = d_1$$

$$a_{21}x + a_{22}y = d_2$$

where the  $a$ 's and  $d$ 's are constants. If we multiply the top equation by  $a_{22}$  and the bottom by  $a_{12}$

$$a_{11}a_{22}x + a_{12}a_{22}y = d_1a_{22}$$

$$a_{12}a_{21}x + a_{12}a_{22}y = d_2a_{12}$$

and then subtract the two equations

$$(a_{11}a_{22}x + \cancel{a_{12}a_{22}y}) - (a_{12}a_{21}x + \cancel{a_{12}a_{22}y}) = d_1a_{22} - d_2a_{12}$$

we can then rearrange and solve for  $x$

$$x = \frac{d_1a_{22} - d_2a_{12}}{a_{11}a_{22} - a_{12}a_{21}}$$

# The Determinant

We can do a similar procedure to solve for  $y$ :

$$y = \frac{d_1 a_{21} - d_2 a_{11}}{a_{11} a_{22} - a_{12} a_{21}}$$

The thing to notice is that the denominator is the same in both cases. This denominator has a special name: **a determinant** and it is denoted as

$$\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = a_{11} a_{22} - a_{12} a_{21}$$

The notation on the left expresses the constants as a matrix ( $2 \times 2$  in our case) and the determinant is determined by multiplying the elements along the two diagonals and subtracting them.

# The Secular Determinant

We are going to solve systems of equations that are homogeneous meaning that the  $d$ 's are going to equal zero:

$$a_{11}x + a_{12}y = 0$$

$$a_{21}x + a_{22}y = 0$$

This means that the solutions for  $x$  and  $y$  look like

$$(a_{11}a_{22} - a_{12}a_{21})x = (0)a_{22} - (0)a_{12}$$

$$(a_{11}a_{22} - a_{12}a_{21})y = (0)a_{21} - (0)a_{11}$$

For  $x$  and  $y$  to yield non-trivial solutions, the determinant of our matrix of constants must equal zero.

$$\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = a_{11}a_{22} - a_{12}a_{21} = 0$$

This is known as a **Secular Determinant**.

# Secular Determinant Example

We will later use secular determinants to solve for the ground state energy of a system. This is illustrated in the following example. Given the following system of equations:

$$(1 - E)x + (4 - E)y = 0$$

$$(2 - E)x + (3 - E)y = 0$$

Invoke the fact that there must be a secular determinant and solve for  $E$ .

# The Ground State Energy of a System

Consider the ground state of some arbitrary system. The Schrödinger Equation can be expressed with its wavefunction  $\psi_0$  and energy  $E_0$ :

$$\hat{H}\psi_0 = E_0\psi_0$$

If we multiply both sides by  $\psi_0^*$  and integrate we get

$$\begin{aligned}\int \psi_0^* \hat{H} \psi_0 dV &= \int \psi_0^* E_0 \psi_0 dV \\ \int \psi_0^* \hat{H} \psi_0 dV &= E_0 \int \psi_0^* \psi_0 dV \\ \frac{\int \psi_0^* \hat{H} \psi_0 dV}{\int \psi_0^* \psi_0 dV} &= E_0\end{aligned}$$

where  $dV$  represents the appropriate volume element. The denominator is left unevaluated as we leave open the possibility that  $\psi_0$  is not normalised.

# The Variational Principle

Pretend that we do not actually know  $\psi_0$ . We attempt to approximate it using a trial wavefunction  $\phi$ . We can calculate the energy of this wavefunction using the same procedure:

$$\frac{\int \phi^* \hat{H} \phi dV}{\int \phi^* \phi dV} = E_\phi$$

**The Variational Principle** states that

$$E_\phi \geq E_0$$

where the equality holds when  $\phi = \psi_0$ . If  $\phi$  is dependent on some parameters (called **variational parameters**) then

$$E_\phi(\alpha, \beta, \gamma, \dots) \geq E_0$$

We can now minimize  $E_\phi$  with respect to each variational parameter and approach  $E_0$



# Variational Principle Example

Apply the Variational Principle using a simple Gaussian function

$$\phi(r) = e^{-\alpha r^2}$$

where  $\alpha$  is the only variational parameter to determine the ground state energy of the hydrogen atom.

# Linear Combinations of Trial Wavefunctions

A trial wavefunction  $\phi$  can also be a linear combination (meaning a sum) of functions ( $f_n$ ) weighted by variational parameters ( $c_n$ ):

$$\phi = \sum_{n=1}^N c_n f_n$$

Furthermore, the functions ( $f_n$ ) can also have variational parameters.

# Ground State Energy of the Hydrogen Atom Revisited

With this in mind we could have used multiple Gaussian functions to guess the ground state energy of the Hydrogen Atom using a trial wavefunction of the form

$$\phi = \sum_{n=1}^N c_n e^{-\alpha_n r^2}$$

where the  $c_n$ 's and the  $\alpha_n$ 's are treated as variational parameters. We have to solve this problem numerically because  $\phi$  does not vary linearly with respect to  $\alpha_n$ , however, with just four terms ( $N = 4$ ), we come to within 99.9% of the correct ground state value.

With multiple terms in our trial wavefunction, we will need to calculate secular determinants in order to solve for unknown variational parameters.

# Summary

- When solving homogeneous systems of equations the determinant must be equal to zero in order for there to be a non-trivial solution for the unknown quantities
- The variational principle uses a trial wavefunction of the form:

$$\phi = \sum_{n=1}^N c_n f_n$$

to approximate the actual wavefunction.

- The energy of the trial wavefunction,  $\phi$  is

$$E_{\phi} = \frac{\int \phi^* \hat{H} \phi dV}{\int \phi^* \phi dV}$$

By minimizing the variational parameters of  $\phi$ , we move closer to the actual ground state energy of a quantum system such that

$$E_{\phi} \geq E_0$$