CH 3006
Advanced Quantum Chemistry

Approximation Methods

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Semester I

Approximation Methods

1. Variation method
2. Perturbation method

Variation method

- Allows us to approximate the ground-state energy of a system without solving the Schrödinger equation.
- Based on the variation theorem.

Variation theorem

Given a system whose Hamiltonian operator $\hat{H}$ is time-independent and whose lowest-energy eigenvalue is E_1, if ϕ is any normalized, well-behaved function of the coordinates of the system's particles that satisfies the boundary conditions of the problem, then,

$$\int \phi^* \ \hat{H} \ \phi \ d\tau \geq \ E_1 \quad (\phi \ normalized)$$

Variation theorem allows us to calculate an upper bound for the system's ground-state energy.

Variation method

- Consider the ground-state of some arbitrary system. Ground-state wave function ψ_0 and energy E_0 satisfy the Schrödinger equation:
  $$\hat{H}\psi_0 = E_0\psi_0$$

- Multiply this from the left by ψ_0^* and integrate over all space:

$$E_0 = \frac{\int \psi_0^* \hat{H} \psi_0 d\tau}{\int \psi_0^* \psi_0 d\tau} = \frac{\langle \psi_0 | \hat{H} | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle}$$

- Variation theorem says that if we substitute any other function ϕ for ψ_0 in the above equation and calculate the corresponding energy according to:

$$E_\phi = \frac{\int \phi^* \widehat{H} \phi d\tau}{\int \phi^* \phi d\tau} = \frac{\langle \phi | \widehat{H} | \phi \rangle}{\langle \phi | \phi \rangle}$$

Then, E_ϕ will be greater than ground state energy E_0.

Examples of the variation method

- Devise a trial variation function for the particle in a 1-D box of length l.

- The variation function ϕ must meet the boundary conditions of being zero at the ends of the box.

- The ground state wave function has no nodes inside the boundary points. It is desirable that the trial function ϕ has no interior nodes.

A simple function with these properties is the parabolic function,

$$\phi = x\,(l - x) \qquad \text{for } 0 \leq x \leq l$$

Determinants

- We will come across n linear algebraic equations in n unknowns. Such equations are best solved by means of determinants.

- Consider the pair of linear algebraic equations.

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

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

- Multiply the first equation by a_{22} and the second by a_{12} and subtract:

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

Determinants

- Similarly multiply first one by a_{21} and second one by a_{11} and then subtract:

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

- Same denominators. Can be represented by a 2×2 determinant.

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

- Generally, a n × n determinant is a square array of n^2 elements arranged in n rows and n columns.

Determinants

- We can define a cofactor.

- The cofactor A_{ij} of an element a_{ij} is a (n-1) × (n-1) determinant obtained by deleting the i^{th} row and the j^{th} column, multiplied by $(-1)^{i+j}$.

- e.g. A_{12} is the cofactor of element a_{12}:

$$D = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix}$$

$$A_{12} = (-1)^{1+2} \begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix}$$

- We use cofactors to evaluate determinants.

- Evaluation by expanding in terms of the first row:

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} = a_{11}A_{11} + a_{12}A_{12} + a_{13}\,A_{13}$$

- e.g. Q.1 of handout

$$D = \begin{vmatrix} 2 & -1 & 1 \\ 0 & 3 & -1 \\ 2 & -2 & 1 \end{vmatrix} = (2)A_{11} + (-1)A_{12} + (1)A_{13} = -2$$

- Evaluate the above, by expanding in terms of the first column of elements (instead of the first row).

- Now try choosing the second row of D.

- A determinant may be evaluated by expanding it in terms of the cofactors of the elements of any row or any column.

Useful properties of determinants

1. The value of a determinant is unchanged if the rows are made into columns in the same order.

e.g. $\begin{vmatrix} 1 & 2 & 5 \\ -1 & 0 & -1 \\ 3 & 1 & 2 \end{vmatrix} = \begin{vmatrix} 1 & -1 & 3 \\ 2 & 0 & 1 \\ 5 & -1 & 2 \end{vmatrix}$

2. If any two rows or columns are the same, the value of the determinant is zero.

$$\begin{vmatrix} 4 & 2 & 4 \\ -1 & 0 & -1 \\ 3 & 1 & 3 \end{vmatrix} = 0$$

3. If any two rows or columns are interchanged, the sign of the determinant is changed. (Interchanging any two rows (or two columns) multiplies the value of a determinant by -1)

$$\begin{vmatrix} 3 & 1 & -1 \\ -6 & 4 & 5 \\ 1 & 2 & 2 \end{vmatrix} = -\begin{vmatrix} 1 & 3 & -1 \\ 4 & -6 & 5 \\ 2 & 1 & 2 \end{vmatrix}$$

4. If every element in a row or a column is multiplied by a factor k, the value of the determinant is multiplied by k.

$$\begin{vmatrix} 6 & 8 \\ -1 & 2 \end{vmatrix} = 2\begin{vmatrix} 3 & 4 \\ -1 & 2 \end{vmatrix}$$

5. If any row or column is written as the sum or difference of two or more terms, the determinant can be written as the sum or difference of two or more determinants.

$$\begin{vmatrix} 3 & 3 \\ 2 & 6 \end{vmatrix} = \begin{vmatrix} 2+1 & 3 \\ -2+4 & 6 \end{vmatrix} = \begin{vmatrix} 2 & 3 \\ -2 & 6 \end{vmatrix} + \begin{vmatrix} 1 & 3 \\ 4 & 6 \end{vmatrix}$$

6. The value of a determinant is unchanged if one row or column is added to or subtracted from another.

(Addition to each element of one row of the same constant multiple of the corresponding element of another row leaves the value of the determinant unchanged. This theorem also applies to the addition of a multiple of one column to another column).

$$\begin{vmatrix} 1 & -1 & 3 \\ 4 & 0 & 2 \\ 1 & 2 & 1 \end{vmatrix} = \begin{vmatrix} 0 & -1 & 3 \\ 4 & 0 & 2 \\ 3 & 2 & 1 \end{vmatrix} = \begin{vmatrix} 0 & -1 & 3 \\ 4 & 0 & 2 \\ 7 & 2 & 3 \end{vmatrix}$$

Add column 2 to column 1

Add row 2 to row 3

7. If every element of a row (or a column) of a determinant is zero, the value of the determinant is zero.

Simultaneous linear algebraic equations

These can be solved in terms of determinants.

Let's consider a pair of equations:

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

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

The determinant of the coefficients of x and y is:

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

Use rule 4 and rule 6 here.

$$x = \frac{\begin{vmatrix} d_1 & a_{12} \\ d_2 & a_{22} \end{vmatrix}}{\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}} \qquad y = \frac{\begin{vmatrix} a_{11} & d_1 \\ a_{21} & d_2 \end{vmatrix}}{\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}}$$

Solutions for x and y in terms of determinants is called Cramer’s rule.

Determinant in the numerator is obtained by replacing the column in D that is associated with the unknown quantity and replacing it with the column associated with the right sides of equations.

Try Q. 2 in the handout. Solve for x, y and z.

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

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

What happens if $d_1 = d_2 = 0$?

?
?
?

The only way to get a non-trivial solution for a set of homogeneous equations is for the denominator to be zero.

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

Secular determinant

In the upcoming lessons we will see equations such as:

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0$$

$$c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) = 0$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = 0$$

The determinant in the above equation is called a secular determinant.

Try Q. 3 in the handout. Solve for λ.

A trial function that depends linearly on the variational parameters leads to a secular determinant

As an example of the variation method, consider a particle in a 1-D box.

One simple function with the properties of the ground-state wave function is $x^n(a-x)^n$ where n is an integer.

Let's assume E_0 by using a trial function:

$$\phi = c_1 x(a-x) + c_2 x^2 (a-x)^2$$

c_1 and c_2 are the variational parameters.

After a lengthy calculation:

$$E_{min} = 0.125002\ \frac{h^2}{ma^2}$$

Compare this with:

$$E_{exact} = \frac{h^2}{8ma^2} = \ 0.125000\ \frac{h^2}{ma^2}$$

If we use a trial function with more than one parameter, it can produce impressive results. But, after a lengthy calculation.

How do we handle such a trial function in a systematic way??

$$\phi = c_1 x(a-x) + c_2 x^2 (a-x)^2$$

Above trial function is a linear combination of functions.

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

c_n are variational parameters

f_n are arbitrary known functions (that at least satisfy boundary conditions)

Assume N = 2 and that c_n and f_n are real.

Consider,

$$\phi = c_1 f_1 + c_2 f_2$$

Show that

$$E\,(c_1, c_2) = \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}}$$

To find an energy closest to the ground state energy, $E\,(c_1, c_2)$ must be minimized with respect to c_1 and c_2.

Differentiate with respect to c_1:

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0$$

Differentiate with respect to c_2:

$$c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) = 0$$

These two equations constitute a pair of linear algebraic equations for c_1 and c_2.

There is a non-trivial solution, that is, a solution that is not simply $c_1 = c_2 = 0$, if and only if the determinant of the coefficient vanishes.

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = 0$$

Therefore we have a secular determinant and a secular equation.

The quadratic secular equation gives two values for E.

We take the smaller of the two as our variational approximation for the ground-state energy.

Try Q. 4 in the handout.