Quantum Chemistry

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Chapter 3

Basic methods of approximation

Except for a very simple case such as a hydrogen atom, the fundamental equation of quantum mechanics cannot be solved rigorously. It follows that approximation mathods should be used to apply quantum mechanics to various problems. Methods to be used as well as the accuracies to be required depend on the problems to be solved.

In this chapter, we will study most imortant and useful methods for approximation.

3.1 Perturbation theory

Even if an equation is difficult to solve directly, true solutions can be deduced from approximate solutions of a slightly simplified equation, provided that the approximate solutions are known or can be obtained easily. Such a technique, based on perturbation theory, is often used for calculations in quantum theory. Perturbation theory is applied to many problems for estimating changes of energy levels and wave functions associated with additional variations due to interparticle interaction as well as magnetic or electric fields.

3.1.1 Perturbation theory

In the equation of quantum mechanics, an additional term $\hat{H}'$ included in the Hamiltonian operator $\hat{H}$ is called a perturbation. A system without perturbation is called the unperturbed system. Assuming that solutions $\{E_i{}^\circ,\, \Psi_i{}^\circ\}$ of the eigen equation $\hat{H}_0\Psi^\circ = E\Psi^\circ$ for the unperturbed Hamiltonian $\hat{H}_0 = \hat{H} - \hat{H}'$ are known, let us try to obtain solutions $\{E_n,\, \Psi_n\}$ of the eigen equation $\hat{H}\Psi = E\Psi$ for the Hamiltonian including the perturbation $\hat{H} = \hat{H}_0 + \hat{H}'$.

First, we introduce a perturbation $\hat{H}' = \lambda\hat{V}$ with a parameter λ indicating the magnitude of the perturbation. Next, we expand Ψ_n in terms of solutions for the unperturbed system $\{\Psi_i{}^\circ\}$.

$$\Psi_n = \sum_i c_{in}\Psi_i{}^\circ \tag{3.1}$$

Insertion of $\hat{H} = \hat{H}_0 + \lambda\hat{V}$ into the eigen equation of $\hat{H}$, followed by using the above expanded equation for Ψ_n and the eigen equation of $\hat{H}_0$, then results in

$$\sum_i c_{in}\{E_i{}^\circ + \lambda\hat{V}\}\Psi_i{}^\circ = E_n \sum_i c_{in}\Psi_i{}^\circ \tag{3.2}$$

Noting that an orthonormal system can be used in general for $\{\Psi_i{}^\circ\}$, multiplication through from the left by $\Psi_j{}^{\circ *}$ and integration yield the following equation.

$$c_{jn}E_j{}^\circ + \lambda\sum_i c_{in}V_{ji} = c_{jn}E_n \tag{3.3}$$

V_{ji} is an integral for all coordinates represented by q, which is give by the following equation.

$$V_{ji} = \int \Psi_j{}^{\circ *}\hat{V}\Psi_i{}^{\circ}\mathrm{d}q \tag{3.4}$$

This quantity V_{ji} can be evaluated when $\{\Psi_i{}^{\circ}\}$ as well as the operator representing the perturbation $\hat{V}$ are given. λV_{ji} is denoted by $H_{ji}{}'$ and is called the ji-matrix element of the perturbation.

$$\begin{aligned} H_{ji}{}' &= \int \Psi_j{}^{\circ *}\hat{H}'\Psi_i{}^{\circ}\mathrm{d}q \\ &= \int \Psi_j{}^{\circ *}\lambda\hat{V}\Psi_i{}^{\circ}\mathrm{d}q \\ &= \lambda V_{ji} \end{aligned} \tag{3.5}$$

This equation will be used for the formula of perturbation theory.

The equation (3.3) is an equation for obtaining energy eigen values E_n and $\{c_{in}\}$ determining the wave functions Ψ_n. In order to solve this equation approximately, let us expand c_{in} and E_n into power series of λ.

$$c_{in} = c_{in}{}^{\circ} + \lambda c_{in}{}' + \lambda^2 c_{in}{}'' + \cdots \tag{3.6}$$

$$E_n = E_n{}^{\circ} + \lambda E_n{}' + \lambda^2 E_n{}'' + \cdots \tag{3.7}$$

When $E_n{}^{\circ}$ has no degeneracy, we obtain $c_{in}{}^{\circ} = \delta_{in}$(1 for $i = n$, 0 for $i \neq n$), since for $\lambda \rightarrow 0$ $\Psi_n \rightarrow \Psi_n{}^{\circ}$ associated with $E_n \rightarrow E_n{}^{\circ}$. Therefore, the first terms in the expansion correspond to the unperturbed system, and the second terms are corrections to the perturbation. Inserting the above expansions eqs.(3.6)(3.7) into eq.(3.3), followed by arranging the lower order terms of λ from the left, we obtain

$$\lambda(V_{nn} - E_n{}') + \lambda^2\left(\sum_i V_{ni}c_{in}{}' - c_{nn}{}'E_n{}' - E_n{}''\right) + \cdots = 0 \tag{3.8}$$

By neglecting the second and the higher order terms, we obtain the following result for the first order correction of the energy.

$$E_n{}' = V_{nn} \tag{3.9}$$

It follows that the formula for the energy to the first order of the perturbation is given by

$$\begin{aligned} E_n \fallingdotseq E_n{}^{\circ} + \lambda V_{nn} &= E_n{}^{\circ} + H'_{nn} \\ &= \int \Psi_n{}^{\circ *}\{\hat{H}_0 + \hat{H}'\}\Psi_n{}^{\circ}\mathrm{d}q \\ &= \int \Psi_n{}^{\circ *}\hat{H}\Psi_n{}^{\circ}\mathrm{d}q \end{aligned} \tag{3.10}$$

The last equation indicates that the expectation value of the Hamiltonian operator including the perturbation in terms of unperturbed wave functions $\Psi_n{}^{\circ}$ yields the energy to the first order of the perturbation.

By considering the second order contributions of λ, we obtain the following equation.

$$E_n{}'' = \sum_{i\,(i\neq n)} V_{ni}c_{in}{}' \tag{3.11}$$

From the first order terms of λ in eq.(3.3) with insertion of expanded expressions, $c_{in}{}'$ $(i \neq n)$ can be written as follows.

$$c_{in}{}' = \frac{V_{in}}{E_n{}^{\circ} - E_i{}^{\circ}} \qquad (i \neq n) \tag{3.12}$$

Using this expression for eq.(3.11) we write

$$E_n{}'' = \sum_{i\,(i\neq n)} \frac{V_{ni}V_{in}}{E_n{}^{\circ} - E_i{}^{\circ}} \tag{3.13}$$

Using the above results, we obtain the following formulas for approximations of $\{E_n, \Psi_n\}$ to the second order of the perturbation.

$$E_n \risingdotseq E_n{}^\circ + H_{nn}{}' + \sum_{i\,(i\neq n)} \frac{H_{ni}{}' H_{in}{}'}{E_n{}^\circ - E_i{}^\circ} \tag{3.14}$$

$$\Psi_n \risingdotseq \Psi_n{}^\circ + \sum_{i\,(i\neq n)} \left(\frac{H_{in}{}'}{E_n{}^\circ - E_i{}^\circ} \right) \Psi_i{}^\circ \tag{3.15}$$

Example 3.1 Verify that second-order perturbation corrections of the energy due to the lower energy states are always positive, whereas those due to the higher energy states are always negative. It should be noted that $H_{ni}{}' = H_{in}{}'^*$, where * denotes the complex conjugate (eq.(1.37)).

(Solution) The second-order perturbation corrections for the energy of the n-th state is expressed by

$$E_n(2) = \sum_{i\,(i\neq n)} \frac{H_{ni}{}' H_{in}{}'}{E_n{}^\circ - E_i{}^\circ}$$

Using $H_{ni}{}' = H_{in}{}'^*$ and noting $|H_{in}{}'|^2 > 0$, we obtain

$$H_{ni}{}' H_{in}{}' = H_{in}{}'^* H_{in}{}' = |H_{in}{}'|^2 > 0$$

This means that the numerators in the expression for $E_n(2)$ are always positive. It follows that contributions due to the lower energy states $i(E_i{}^\circ < E_n{}^\circ)$ are always positive.

$$\frac{H_{ni}{}' H_{in}{}'}{E_n{}^\circ - E_i{}^\circ} > 0$$

Also, contributions due to the higher energy states $i(E_i{}^\circ > E_n{}^\circ)$ are always negative.

$$\frac{H_{ni}{}' H_{in}{}'}{E_n{}^\circ - E_i{}^\circ} < 0$$

3.1.2 Perturbation theory for degenerate states

Now let us consider a system with f-fold degeneracy in the energy E°. The degenerate states are numbered from 1 to f , and energies of these degenerate states are denoted as $E_1{}^\circ = E_2{}^\circ = \cdots = E_f{}^\circ$. For any other state a number n larger than f is assigned. For the energy levels of $n > f$, $\{E_n, \Psi_n\}$ are obtained by the method studied above. The energy levels from 1 to f should be treated differently, noting that $E_n \to E_n{}^\circ$ and $\Psi_n \to \sum_{i=1}^{f} c_{in}{}^\circ \Psi_i{}^\circ$, associated with $\lambda \to 0$. Insertion of equations (3.6) and (3.7) into eq.(3.3), followed by neglecting higher order terms than the second order of λ, results in the following a set of simultaneous equations.

$$\sum_{i=1}^{f} (V_{ji} - \delta_{ji} E_n{}') c_{in}{}^\circ = 0 \tag{3.16}$$

where j and n are arbitrary numbers from 1 to f.

According to linear algebra, the necessary and sufficient condition for the existence of nontrivial solutions other than all $\{c_{in}{}^\circ\}$ to be vanishing is that the determinant of the matrix with ji element corresponding to the inside of ( ) in eq.(3.16) should be zero.

$$\begin{vmatrix} V_{11} - E_n{}' & V_{12} & V_{13} & \cdots & V_{1f} \\ V_{21} & V_{22} - E_n{}' & V_{23} & \cdots & V_{2f} \\ V_{31} & V_{32} & V_{33} - E_n{}' & \cdots & V_{3f} \\ \vdots & \vdots & \vdots & & \vdots \\ V_{f1} & V_{f2} & V_{f3} & \cdots & V_{ff} - E_n{}' \end{vmatrix} = 0 \tag{3.17}$$

By solving this algebraic equation of the order f with respect to $E_n{}'$, f solutions of $E_1{}', E_2{}', \cdots, E_f{}'$ can be obtained. Thus, the energy levels shifted by the perturbation can be determined as follows.

$$E_n \fallingdotseq E_n{}^\circ + \lambda E_n{}' \qquad (1 \leqq n \leqq f) \tag{3.18}$$

$\{c_{in}{}^\circ\}$ can also be obtained from solutions of the simultaneous equations of (3.16), provided that a value of $\{E_n{}'\}$ from eq.(3.17) is inserted in place of $E_n{}'$ in ( ). It should be noted that the following equation for the normalization condition for $\{\Psi_n\}$.

$$\sum_{i=1}^{f} |c_{in}{}^\circ|^2 = 1 \qquad (1 \leqq n \leqq f) \tag{3.19}$$

3.1.3 Modification of states by perturbation

Modification of energy levels due to additional actions can be observed as spectral changes for transitions related to the levels. We will see some typical examples below.

[The Zeeman effect]

When magnetic fields are applied, doublet or triplet states may exhibit the splitting of degenerate energy levels. Phenomena of the splitting in spectral lines under magnetic fields are called the Zeeman effect. The extent of the splitting of spectral lines depends on the strength of the applied field. Fig.3.1 shows an example of the Zeeman effect on the $^1D_2$–$^1P_1$ transition giving red emission (6438.47 Å) from a cadmium atom. One line without a field splits into three lines under the magnetic field.

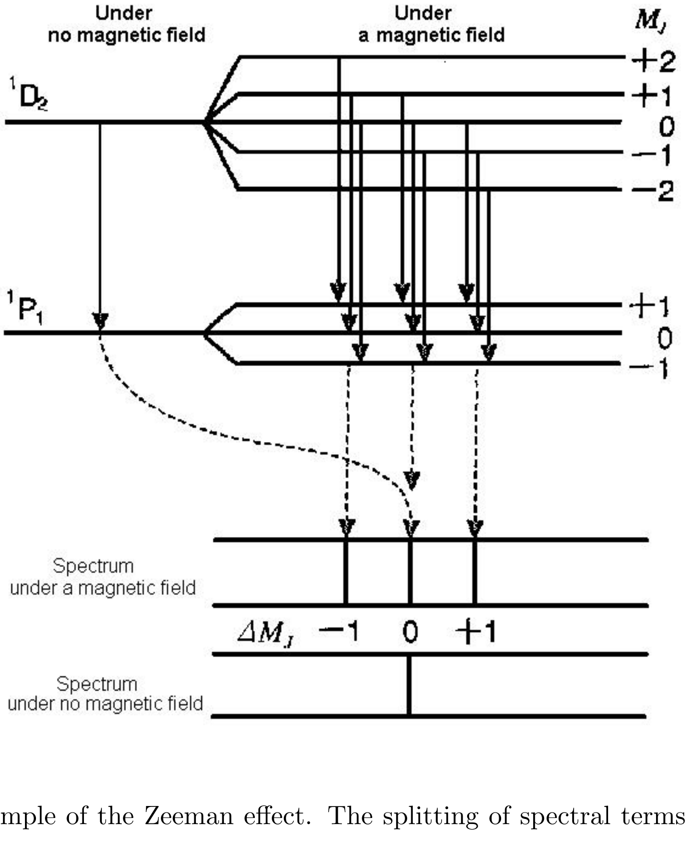

Figure 3.1: An example of the Zeeman effect. The splitting of spectral terms under a magnetic field

[The Stark effect]

Emission spectra from a hydrogen atom in a strong electric field give splitting of spectral lines. The splitting of spectral lines under an electric field is called the Stark effect. The Stark effect is observed for the following cases.

(1) At least one of the energy levels related to the transition is degenerate, and the degeneracy is lifted by the action of the electric field.

(2) Polar molecules with various orientation may have different energies under a strong electric field, and transition energies may also be modified depending on the molecular orientation.

The latter type of the Stark effect does not require the degeneracy of the levels. The extent of the splitting in the Stark effect depends on the strength of the applied electric field.

[The splitting of d levels]

Levels of d electrons in a metal atom or its ion (M) exhibit varieties of split patterns under the field (ligand field or crystal field) of the surrounding ligands (L), depending on the symmetry and the field strengths (Fig.3.2). Subtle changes in color for transition metal ions and their compounds are related to the variations of split patterns of d levels.

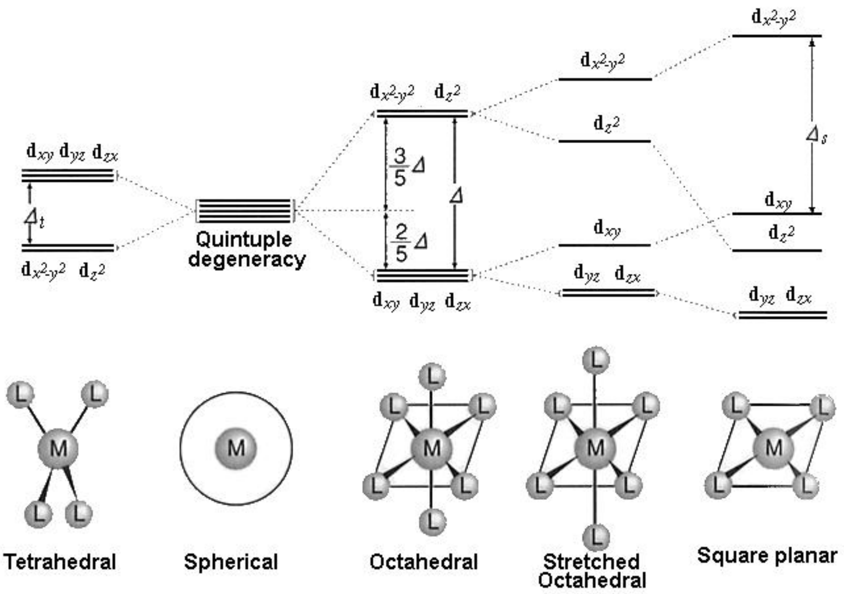

Figure 3.2: The ligand field splitting of d levels. M: central metal, L: ligand.

[Spin-orbit coupling effects]

As studied in section 2.7, levels with the same set of L and S are degenerate, when the spin-orbit coupling can be disregarded. If the spin-orbit coupling is significant, especially for atoms with large atomic numbers to which relativistic effects cannot be neglected, the degeneracy is lifted to give splitting of spectral lines. Multiplet states such as doublets and triplets can be observed as split states even without external fields, and such a phenomenon is called the zero-field splitting in contrast to the Zeeman effect.

[The transition probability and spectral selection rules]

In addition to the above examples, rapid variations such as actions due to electromagnetic waves can also be treated as a perturbation. Since systems under actions of electromagnetic waves are not in stationary states, theoretical treatments of unstationary states need to be made. Although details will not be mentioned in this book, an extension of perturbation theory to unstationary states makes it possible to evaluate the transition probabilities between stationary states. Looking into the transition probabilities reveals that transitions do not necessarily occur between any pair of states. There are certain rules which lead to either allowed transitions or forbidden transitions.

For example, the following selection rules are well known as conditions in order to observe light absorption or emission by atoms.

$$\begin{aligned}
&\Delta L = 0 \,\text{or}\, \pm 1 && \text{(The selection rule for orbital angular momenta)} \\
&\Delta J = 0 \,\text{or}\, \pm 1 && \text{(The selection rule for total angular momenta)} \\
&\Delta S = 0 && \text{(The selection rule for spin angular momenta)}
\end{aligned} \tag{3.20}$$

Exceptionally, $\Delta L = 0$ should be omitted between a pair of states with $L = 0$, and also $\Delta J = 0$ should be omitted between a pair of states with $J = 0$. When transitions do not satisfy the conditions in eq.(3.20), the corresponding spectral lines cannot be observed or appear with extremely weak intensities, even if they could be observed. The last rule of $\Delta S = 0$, forbidding transitions between levels with different spin-multiplicity becomes to be less effective with the increase of the atomic number, since the spin-orbit coupling becomes to be strong for heavy atoms.

As can be seen from Fig.3.1, among transitions between split sublevels due to the difference of the M_J values, transitions of $\Delta M_J = 0$ or ± 1 are only allowed.

3.2 The variation method

Besides the perturbation method studied in the previous section, another approach called the variation method has been used for applying quantum mechanics to various problems. Especially in recent years, development of modern computers has facilitated valuable usage of calculation methods based on the variation method. In this section we will study the variation method. Now, let us start with the variation principle.

3.2.1 The variation principle

A trial expectation value with an arbitrary function Φ is introduced by the following equation.

$$\varepsilon[\Phi] = \frac{\int \Phi^* \hat{H} \Phi \mathrm{d}q}{\int \Phi^* \Phi \mathrm{d}q}. \tag{3.21}$$

The value of $\varepsilon[\Phi]$ which depends on the choice of Φ is not smaller than the lowest eigen value E_0 for the eigen equation $\hat{H}\Psi = E\Psi$.

$$\varepsilon[\Phi] \geqq E_0 \qquad \text{(The equality holds only if } \hat{H}\Phi = E_0\Phi\text{)} \tag{3.22}$$

The equality of this formula holds only for a special case where $\varepsilon[\Phi]$ is an eigen function belonging to E_0. This formula of eq.(3.22) is called the variation principle.

[Proof]

Φ can be expanded in terms of eigen functions $\{\Psi_i\}$ for $\hat{H}$ as $\Phi = \sum\limits_i c_i \Psi_i$. Calculating $\varepsilon[\Phi] - E_0$ with the expansion of Φ and using $\hat{H}\Psi_i = E_i \Psi_i$ as well as the normality of $\{\Psi_i\}$, we obtain

$$\varepsilon[\Phi] - E_0 = \frac{\sum\limits_i (E_i - E_0)|c_i|^2 \int |\Psi_i|^2 \mathrm{d}q}{\sum\limits_i |c_i|^2 \int |\Psi_i|^2 \mathrm{d}q} \geqq 0.$$

The last inequality is derived from the followings; E_0 is the lowest eigen value, and an absolute value cannot be negative. Since $\{\Psi_i\}$ cannot be zero for all possible cases of the variables, the equality requires $c_i = 0$ for all $\{\Psi_i\}$ having an energy E_i larger than E_0. It follows that a nonzero value for the coefficient c_i in the expansion of Φ in terms of $\{\Psi_i\}$ is allowed only if $E_i = E_0$. Only in this case, $\hat{H}\Phi = E_0\Phi$ holds, and Φ becomes the eigen function belonging to the eigen value E_0. Conversely, if Φ is an eigen function of E_0 satisfying $\hat{H}\Phi = E_0\Phi$, the numerator of eq.(3.21) becomes $\int \Phi^* E_0 \Phi \mathrm{d}q = E_0 \int \Phi^* \Phi \mathrm{d}q$, which leads to $\varepsilon[\Phi] = E_0$. Therefore, the equality holds only if $\hat{H}\Phi = E_0\Phi$, which is the case that Φ is the eigen function of the lowest eigen value E_0.

The variation principle gives a guide to obtain the wave function and the eigen value of the ground-state. For this purpose, Φ should be determined so that the value of $\varepsilon[\Phi]$ using Φ may become the minimum. The resultant Φ is the eigen function of the lowest eigen value E_0, the wave function of the ground-state. It follows that this Φ yields $\varepsilon[\Phi]$ corresponding to the ground-state energy value of E_0.

3.2.2 The variation method using a linear-combination approximation (Ritz's variation method)

It is difficult to find out Φ minimizing $\varepsilon[\Phi]$ on the basis of the above variation principle. For various functions ϕ_1, ϕ_2, ϕ_3, $\cdots$, we need to calculate the respective value of $\varepsilon[\phi_i]$, and we should find out a function giving the minimum. It is however impossible to test all functions. Even if several combinations of E and Ψ satisfying $\hat{H}\Psi = E\Psi$, the lowest eigen value among them is not necessarily the true minimum eigen value. Therefore, a compromise of finite numbers of trials giving up infinite repetitions would lead to unsuccessful results unless fortunate choices happened to be made.

Now, let us try to test a wide range of functions more efficiently. A linear combination of n functions ϕ_1, ϕ_2, ϕ_3, $\cdots$, ϕ_n

$$\Phi = c_1\phi_1 + c_2\phi_2 + \cdots + c_n\phi_n \tag{3.23}$$

can be used to test infinite numbers of trial functions expressed by eq.(3.23), provided that expansion coefficients $\{c_i\}$ as adjustable variables are continuously varied. Although there is a restriction due to the selection of $\{\phi_i\}$, we can obtain the best result for testing all of arbitrary linear combinations of $\{\phi_i\}$ as well as individual functions from ϕ_1 to ϕ_n. In this way, the variation principle is used to determine a series of $\{c_i\}$ so that $\{c_i\}$ may lead to the minimum of $\varepsilon[\Phi]$. This procedure is called the variation method using a linear-combination approximation (Ritz's variation method).

Insertion of eq.(3.23) into the definition of $\varepsilon[\Phi]$ leads to the following equation.

$$\varepsilon[\Phi] = \frac{\sum\limits_i \sum\limits_j {c_i}^* H_{ij} c_j}{\sum\limits_i \sum\limits_j {c_i}^* S_{ij} c_j} \tag{3.24}$$

In this expression summations for i and j should be taken from 1 to n. H_{ij} and S_{ij} are elements of $n \times n$ matrices and defined by the following integrals.

$$H_{ij} = \int {\phi_i}^* \hat{H} \phi_j \mathrm{d}q \tag{3.25}$$

$$S_{ij} = \int {\phi_i}^* \phi_j \mathrm{d}q \tag{3.26}$$

S_{ij} is called an overlap integral between ϕ_i and ϕ_j.

Based on the variation principle, $\varepsilon[\Phi]$ should be minimized by changing $\{c_i\}$, which are the coefficients introduced in the definition of Φ. Since c_i and c_i^* are complex conjugates with each other, we may take one of them as an independent variable. Hence, let us obtain the condition for $\partial\varepsilon/\partial {c_i}^* = 0$. For convenience, we rewrite eq.(3.24) as

$$\varepsilon[\Phi] \sum_i \sum_j {c_i}^* S_{ij} c_j = \sum_i \sum_j {c_i}^* H_{ij} c_j \tag{3.27}$$

Differentiation of the both sides of this equation with respect to ${c_i}^*$ gives

$$\frac{\partial\varepsilon}{\partial {c_i}^*} \sum_i \sum_j {c_i}^* S_{ij} c_j + \varepsilon \sum_j S_{ij} c_j = \sum_j H_{ij} c_j \tag{3.28}$$

Using the condition of $\partial\varepsilon/\partial {c_i}^* = 0$, we obtain

$$\sum_j (H_{ij} - \varepsilon S_{ij}) c_j = 0 \qquad (i = 1, 2, \cdots, n) \tag{3.29}$$

This expression is a set of simultaneous equations for $\{c_j\}$, which is similar to eq.(3.16) in the previous section.

If all coefficients from c_1 to c_n are zero, then they satisfy eq.(3.29). However, this set of solutions leads to an identity of $\Phi = 0$, which is physically of no meaning. In order to obtain nontrivial solutions other than all $\{c_j\}$ to be vanishing, the following determinant should be zero.

$$\begin{vmatrix} H_{11}-\varepsilon S_{11} & H_{12}-\varepsilon S_{12} & \cdots & H_{1n}-\varepsilon S_{1n} \\ H_{21}-\varepsilon S_{21} & H_{22}-\varepsilon S_{22} & \cdots & H_{2n}-\varepsilon S_{2n} \\ \vdots & \vdots & & \vdots \\ \vdots & \vdots & & \vdots \\ H_{n1}-\varepsilon S_{n1} & H_{n2}-\varepsilon S_{n2} & \cdots & H_{nn}-\varepsilon S_{nn} \end{vmatrix} = 0 \tag{3.30}$$

The ij elements A_{ij} of this determinant is derived from the coefficients of $(H_{ij} - \varepsilon S_{ij}) = A_{ij}$ in the simultaneous equations (3.29). Eq.(3.30) is an algebraic equation of the order n for ε, and it is called the secular equation. The secular equation is simply expression as $|H_{ij} - \varepsilon S_{ij}| = 0$, in which only the ij element is written between a pair of vertical bars. $\varepsilon_1, \varepsilon_2, \cdots, \varepsilon_n (\varepsilon_i \leqq \varepsilon_{i+1})$ are n solutions of this equation and approximate energy eigen values. The lowest eigen value ε_1 is the best approximation of the true ground-state energy within all possible ranges of the linear combination for Φ in eq.(3.23). In comparison with true eigen values from the lower ones, $E_1, E_2, E_3, \cdots$, the eigen values obtained by Ritz's variation method satisfy the following relation.

$$E_k \leqq \varepsilon_k \qquad (k = 1, 2, \cdots, n) \tag{3.31}$$

Therefore, ε_k $(k \geqq 2)$ is an approximate energy value for the k-th excited state.

Wave functions $\{\Phi_k\}$ corresponding to the approximate energy eigen values $\{\varepsilon_k\}$ can be determined by insertion of ε_k into the simultaneous equations (3.29), followed by obtaining $\{c_j\}$. It should be noted here that the normalization condition leads to the following equation to be satisfied for $\{c_j\}$.

$$\int \Phi_k{}^* \Phi_k \mathrm{d}q = \sum_i \sum_j c_i{}^* c_j S_{ij} = 1 \tag{3.32}$$

Example 3.2 Calculate approximate energies and wave functions by applying Ritz' variation method to $\Phi = c_1\phi_1 + c_2\phi_2$, provided that $H_{11} = -12\,\mathrm{eV}$, $H_{22} = -6\,\mathrm{eV}$, $H_{12} = H_{21} = -4\,\mathrm{eV}$, $S_{11} = S_{22} = 1$, $S_{12} = S_{21} = 0$.

(Solution) Using the given conditions, the secular equation is expressed by

$$\begin{vmatrix} -12-\varepsilon & -4 \\ -4 & -6-\varepsilon \end{vmatrix} = \varepsilon^2 + 18\varepsilon + 56 = (\varepsilon + 14)(\varepsilon + 4) = 0$$

The lower solution gives the ground-state energy of $\varepsilon_1 = -14\,\mathrm{eV}$, and the higher one corresponds to the excited-state energy of $\varepsilon_2 = -4\,\mathrm{eV}$.

The wave function Φ can be obtained in the following way. Applying the given conditions to the normalization condition of eq.(3.32),

$$|c_1|^2 + |c_2|^2 = 1 \tag{1}$$

Simultaneous equations (3.29) for coefficients c_1, c_2 give

$$(H_{11} - \varepsilon)c_1 + H_{12}c_2 = 0 \tag{2}$$

Insertion of values for H_{11}, H_{12} and ε_1 into this equation (2) leads to

$$(-12 + 14)c_1 + (-4)c_2 = 0$$

This yields $c_1 = 2c_2$, and then eq.(1) gives $c_1 = 2/\sqrt{5}$, $c_2 = 1/\sqrt{5}$. Thus, we obtain the ground-state wave function.

$$\Phi_1 = \frac{1}{\sqrt{5}}(2\phi_1 + \phi_2)$$

Next, insertion of ε_2 into ε in eq.(2) leads to

$$(-12 + 4)c_1 + (-4)c_2 = 0$$

This yields $2c_1 = -c_2$, and then eq.(1) gives $c_1 = 1/\sqrt{5}$, $c_2 = -2/\sqrt{5}$. Thus we obtain the excited-state wave function.

$$\Phi_2 = \frac{1}{\sqrt{5}}(\phi_1 - 2\phi_2)$$

3.3 The SCF method

As studied in section 2.4, wave functions for many electrons systems can be constructed with orbital functions. The problem is how to determine orbital function for many electron systems. In this section, we study a fundamental approach obtaining orbital functions on the basis of the variation method.

The Hamiltonian operator for an n electron system is given by the following expression.

$$\hat{H} = \sum_{i=1}^{n} \hat{h}(i) + \sum_{i>j}^{n} \hat{g}(i,j) \tag{3.33}$$

Here, $\hat{h}(i)$ and $\hat{g}(i,j)$ are one and two electron operators, respectively. The indices i and j refer to the respective electrons. A comparison of this equation with the formula (2.31) for many electron system in section 2.3 leads to the following expressions for the above operators.

$$\hat{h}(i) = -\frac{\hbar^2}{2m}\Delta_i - \frac{Ze^2}{4\pi\varepsilon_0 r_i} \tag{3.34}$$

$$\hat{g}(i,j) = \frac{e^2}{4\pi\varepsilon_0 r_{ij}} \tag{3.35}$$

Orthonormal orbital functions including spins $\{\psi_i\}$ can be determined from the following simultaneous equations derived from the minimization conditions for the expectation value of $\hat{H}$ by a determinant wave function $\Psi = |\psi_1\psi_2\cdots\psi_n|$ composed of the orbital functions.

$$\begin{aligned}&\left[\hat{h}(i) + \sum_{k}\int \hat{g}(i,j)|\psi_k(j)|^2 \mathrm{d}q_j\right]\psi_i(i) - \sum_{k}\left[\int \hat{g}(i,j)\psi_k{}^*(j)\psi_i(j)\mathrm{d}q_j\right]\psi_k(i)\\ &= \varepsilon_i\psi_i(i) \qquad (i = 1, 2, \cdots, n)\end{aligned} \tag{3.36}$$

The summation should be taken from 1 to n except for $k = i$. Eq.(3.36) is called the Hartree-Fock equation, and solutions of this equation yield the orbital functions $\{\psi_i\}$ and the orbital energies $\{\varepsilon_i\}$.

A sophisticated approach needs to be used for solving eq.(3.36). First, we assume that an approximate set of solutions (the 0-th approximation) for $\{\psi_i\}$ is given. Replacement of ψ_k in the left of eq.(3.36) by the 0-th approximation leads to a simple equation to be solved as follows.

$$\hat{F}\psi = \varepsilon\psi \tag{3.37}$$

Although the approximate solutions of $\{\psi_i\}$ are included in the operator $\hat{F}$, $\{\psi_i\}$ to be determined are not included. It follows that eq.(3.37) can be solved as a normal eigen value equation. Although the first solutions so obtained for $\{\psi_i\}$ and $\{\varepsilon_i\}$, are approximate ones, they are expected to be better than those of the initial guess. Next, we estimate the operator $\hat{F}$ with the first solutions, and then we solve eq.(3.37) again to obtain the second solutions. In such procedures, we improve the solutions iteratively until discrepancies between the results and the assumptions will become negligibly small. It is called self-consistent when the assumed ψ as an approximation becomes consistent with the obtained ψ as a solution. In the convergent solutions, interactions between electrons included in $\hat{F}$ are the self-consistent field. Such a procedure obtaining solutions in an iterative way is the SCF method, and the solutions are called SCF solutions. Orbital functions determined by the SCF method are called SCF orbitals.

Construction of the determinant wave function with the lower-energy SCF orbitals, followed by calculation of the expectation value of the Hamiltonian operator of eq.(3.33), yields an approximation of the ground-state energy, which is called the SCF energy. The SCF energy E_{SCF} is expressed in terms of some integrals by the following equation.

$$E_{\mathrm{SCF}} = \sum_{i}(h)_i + \frac{1}{2}\sum_{i,j}\{(J)_{ij} - (K)_{ij}\} \tag{3.38}$$

The summation should be taken for all occupied orbitals. The integrals for the SCF orbitals including spins are defined as follows.

$$
\begin{aligned}
(h)_i &= \int \psi_i{}^* \hat{h}(i)\psi_i \mathrm{d}q \\
(J)_{ij} &= \int \psi_i{}^*(1)\psi_j{}^*(2)\hat{g}(1,2)\psi_i(1)\psi_j(2)\mathrm{d}q_1\mathrm{d}q_2 \\
(K)_{ij} &= \int \psi_i{}^*(1)\psi_j{}^*(2)\hat{g}(1,2)\psi_j(1)\psi_i(2)\mathrm{d}q_1\mathrm{d}q_2
\end{aligned}
$$

The SCF energy is expressed in terms of individual orbital energies $\{\varepsilon_i\}$ as follows.

$$
E_{\mathrm{SCF}} = \sum_i \varepsilon_i - \frac{1}{2}\sum_{i,j}\{(J)_{ij} - (K)_{ij}\} \tag{3.39}
$$

This indicates that the SCF energy is not equal to the summation of the orbital energies. The additional term is identical with the second term in eq.(3.38) except for the opposite signs. This term is due to the interactions between electrons. The sum of orbital energies includes duplicated contributions of interactions between electrons, since an interaction between a particular couple of two electrons appears in both of the respective orbital energies of the pair of the electrons. It follows that in eq.(3.39) the interactions between electrons multiplied by -1 are added to the sum of the orbital energies. If the interactions between electrons can be neglected, the total energy becomes the sum of individual orbital energies, and the situation is the same as the independent particle model studied in section2.3.

A comparison of the SCF energy with the ground-state energy E_{G} without including relativistic effects such as the spin-orbit coupling leads to the following inequality.

$$
E_{\mathrm{G}} \leqq E_{\mathrm{SCF}}
$$

The equality is only for one-electron systems such as hydrogenic atoms. The equality does not hold for many electron systems. The difference of $E_{\mathrm{SCF}} - E_{\mathrm{G}} = E_{\mathrm{CORR}}$ for many electron systems are always positive. Its magnitude $E_{\mathrm{CORR}}$is called the electron correlation energy. Such a discrepancy is due to the construction of the many-electron wave function from orbitals for independent motion of electrons, which excludes effects of the electron correlation. The variation method as well as the perturbation method may be used to consider electron correlation effects (see section 4.3). In conclusion of this chapter, characteristic features for the perturbation method and the variation method are listed in Table 3.1.

Table 3.1: Characteristic features for the perturbation method and the variation method

	Perturbation method	Variation method
Approach	True solutions are guessed as series expansions with unperturbed solutions, if they are known.	Trial wave functions with adjustable parameters are assumed and optimized to minimize the expectation value.
Feature	If the perturbation is weak, even the lower order expansions give successful results. When the perturbation is strong, slow convergence makes calculations of higher order terms formidable.	Trial functions similar to the true solution give excellent results. If the adjustable range of trail functions is too large, calculations become formidable.

Exercises

3.1 Based on the variation principle, verify that the energy up to the first order of a perturbation $E(1)$ is higher than the true ground-state energy E_{G}.

3.2 For a system of two levels, verify that the higher state goes up and that the lower state comes down, by considering energy corrections due to the second order perturbation.

3.3 Applying Ritz's variation method to $\Phi = c_1\phi_1 + c_2\phi_2$, obtain approximate solutions for the energies and the wave functions, using $H_{11} = H_{22} = -6\,\mathrm{eV},\ H_{12} = H_{21} = -3\,\mathrm{eV},\ S_{11} = S_{22} = 1,\ S_{12} = S_{21} = 0$.