VALENCE BOND METHODS

Theory and applications

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1

Introduction

1.1 History

In physics and chemistry making a direct calculation to determine the structure or properties of a system is frequently very difficult. Rather, one assumes at the outset an ideal or asymptotic form and then applies adjustments and corrections to make the calculation adhere to what is believed to be a more realistic picture of nature. The practice is no different in molecular structure calculation, but there has developed, in this field, two different "ideals" and two different approaches that proceed from them.

The approach used first, historically, and the one this book is about, is called the valence bond (VB) method today. Heitler and London[8], in their treatment of the H_2 molecule, used a trial wave function that was appropriate for two H atoms at long distances and proceeded to use it for all distances. The ideal here is called the "separated atom limit". The results were qualitatively correct, but did not give a particularly accurate value for the dissociation energy of the H−H bond. After the initial work, others made adjustments and corrections that improved the accuracy. This is discussed fully in Chapter 2. A crucial characteristic of the VB method is that the orbitals of different atoms must be considered as nonorthogonal.

The other approach, proposed slightly later by Hund[9] and further developed by Mulliken[10] is usually called the molecular orbital (MO) method. Basically, it views a molecule, particularly a diatomic molecule, in terms of its "united atom limit". That is, H_2 is a He atom (not a real one with neutrons in the nucleus) in which the two positive charges are moved from coinciding to the correct distance for the molecule.[1] HF could be viewed as a Ne atom with one proton moved from the nucleus out to the molecular distance, etc. As in the VB case, further adjustments and corrections may be applied to improve accuracy. Although the united atom limit is not often mentioned in work today, its heritage exists in that MOs are universally considered to be mutually orthogonal. We touch only occasionally upon MO theory in this book.

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[1] Although this is impossible to do in practice, we can certainly calculate the process on paper.

As formulated by Heitler and London, the original VB method, which was easily extendible to other diatomic molecules, supposed that the atoms making up the molecule were in (high-spin) *S* states. Heitler and Rumer later extended the theory to polyatomic molecules, but the atomic *S* state restriction was still, with a few exceptions, imposed. It is in this latter work that the famous Rumer[11] diagrams were introduced. Chemists continue to be intrigued with the possibility of correlating the Rumer diagrams with bonding structures, such as the familiar Kekulé and Dewar bonding pictures for benzene.

Slater and Pauling introduced the idea of using whole atomic configurations rather than *S* states, although, for carbon, the difference is rather subtle. This, in turn, led to the introduction of hybridization and the maximum overlap criterion for bond formation[1].

Serber[12] and Van Vleck and Sherman[13] continued the analysis and introduced symmetric group arguments to aid in dealing with spin. About the same time the Japanese school involving Yamanouchi and Kotani[14] published analyses of the problem using symmetric group methods.

All of the foregoing work was of necessity fairly qualitative, and only the smallest of molecular systems could be handled. After WWII digital computers became available, and it was possible to test many of the qualitative ideas quantitatively.

In 1949 Coulson and Fisher[15] introduced the idea of nonlocalized orbitals to the VB world. Since that time, suggested schemes have proliferated, all with some connection to the original VB idea. As these ideas developed, the importance of the spin degeneracy problem emerged, and VB methods frequently were described and implemented in this context. We discuss this more fully later.

As this is being written at the beginning of the twenty-first century, even small computers have developed to the point where *ab initio* VB calculations that required "supercomputers" earlier can be carried out in a few minutes or at most a few hours. The development of parallel "supercomputers", made up of many inexpensive personal computer units is only one of the developments that may allow one to carry out ever more extensive *ab initio* VB calculations to look at and interpret molecular structure and reactivity from that unique viewpoint.

1.2 Mathematical background

Data on individual atomic systems provided most of the clues physicists used for constructing quantum mechanics. The high spherical symmetry in these cases allows significant simplifications that were of considerable usefulness during times when procedural uncertainties were explored and debated. When the time came to examine the implications of quantum mechanics for molecular structure, it was immediately clear that the lower symmetry, even in diatomic molecules, causes significantly greater difficulties than those for atoms, and nonlinear polyatomic molecules are considerably more difficult still. The mathematical reasons for this are well understood, but it is beyond the scope of this book to pursue these questions. The interested reader may investigate many of the standard works detailing the properties of Lie groups and their applications to physics. There are many useful analytic tools this theory provides for aiding in the solution of partial differential equations, which is the basic mathematical problem we have before us.

1.2.1 Schrödinger's equation

Schrödinger's space equation, which is the starting point of most discussions of molecular structure, is the partial differential equation mentioned above that we must deal with. Again, it is beyond the scope of this book to give even a review of the foundations of quantum mechanics, therefore, we assume Schrödinger's space equation as our starting point. Insofar as we ignore relativistic effects, it describes the energies and interactions that predominate in determining molecular structure. It describes in quantum mechanical terms the kinetic and potential energies of the particles, how they influence the wave function, and how that wave function, in turn, affects the energies. We take up the potential energy term first.

Coulomb's law

Molecules consist of electrons and nuclei; the principal difference between a molecule and an atom is that the latter has only one particle of the nuclear sort. Classical potential theory, which in this case works for quantum mechanics, says that Coulomb's law operates between charged particles. This asserts that the potential energy of a pair of spherical, charged objects is

$$V(|\vec{r}_1 - \vec{r}_2|) = \frac{q_1 q_2}{|\vec{r}_1 - \vec{r}_2|} = \frac{q_1 q_2}{r_{12}}, \tag{1.1}$$

where q_1 and q_2 are the charges on the two particles, and r_{12} is the scalar distance between them.

Units

A short digression on units is perhaps appropriate here. We shall use either Gaussian units in this book or, much more frequently, Hartree's atomic units. Gaussian units, as far as we are concerned, are identical with the old cgs system of units with the added proviso that charges are measured in unnamed *electrostatic units*, esu. The value of $|e|$ is thus $4.803206808 \times 10^{-10}$ esu. Keeping this number at hand is all that will be required to use Gaussian units in this book.

Hartree's atomic units are usually all we will need. These are obtained by assigning mass, length, and time units so that the mass of the electron, $m_e = 1$, the electronic charge, $|e| = 1$, and Planck's constant, $\hbar = 1$. An upshot of this is that the Bohr radius is also 1. If one needs to compare energies that are calculated in atomic units (hartrees) with measured quantities it is convenient to know that 1 hartree is 27.211396 eV, 6.27508×10^5 cal/mole, or 2.6254935×10^6 joule/mole. The reader should be cautioned that one of the most common pitfalls of using atomic units is to forget that the charge on the electron is -1. Since equations written in atomic units have no m_es, es, or $\hbar$s in them explicitly, their being all equal to 1, it is easy to lose track of the signs of terms involving the electronic charge. For the moment, however, we continue discussing the potential energy expression in Gaussian units.

The full potential energy

One of the remarkable features of Coulomb's law when applied to nuclei and electrons is its additivity. The potential energy of an assemblage of particles is just the sum of all the pairwise interactions in the form given in Eq. (1.1). Thus, consider a system with K nuclei, $\alpha = 1, 2, \ldots, K$ having atomic numbers Z_α. We also consider the molecule to have N electrons. If the molecule is uncharged as a whole, then $\sum Z_\alpha = N$. We will use lower case Latin letters, $i, j, k, \ldots$, to label electrons and lower case Greek letters, $\alpha, \beta, \gamma, \ldots$, to label nuclei. The full potential energy may then be written

$$V = \sum_{\alpha<\beta} \frac{e^2 Z_\alpha Z_\beta}{r_{\alpha\beta}} - \sum_{i\alpha} \frac{e^2 Z_\alpha}{r_{i\alpha}} + \sum_{i<j} \frac{e^2}{r_{ij}}. \tag{1.2}$$

Many investigations have shown that any deviations from this expression that occur in reality are many orders of magnitude smaller than the sizes of energies we need be concerned with.[2] Thus, we consider this expression to represent exactly that part of the potential energy due to the charges on the particles.

The kinetic energy

The kinetic energy in the Schrödinger equation is a rather different sort of quantity, being, in fact, a differential operator. In one sense, it is significantly simpler than the potential energy, since the kinetic energy of a particle depends only upon what it is doing, and not on what the other particles are doing. This may be contrasted with the potential energy, which depends not only on the position of the particle in question, but on the positions of all of the other particles, also. For our molecular system the kinetic energy operator is

---

[2] The first correction to this expression arises because the transmission of the electric field from one particle to another is not instantaneous, but must occur at the speed of light. In electrodynamics this phenomenon is called a *retarded potential*. Casimir and Polder[16] have investigated the consequences of this for quantum mechanics. The effect within distances around 10^{-7} cm is completely negligible.

$$T = -\sum_{\alpha} \frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2, \tag{1.3}$$

where M_α is the mass of the α^{th} nucleus.

The differential equation

The Schrödinger equation may now be written symbolically as

$$(T + V)\Psi = E\Psi, \tag{1.4}$$

where E is the numerical value of the total energy, and Ψ is the wave function. When Eq. (1.4) is solved with the various constraints required by the rules of quantum mechanics, one obtains the total energy and the wave function for the molecule. Other quantities of interest concerning the molecule may subsequently be determined from the wave function.

It is essentially this equation about which Dirac[17] made the famous (or infamous, depending upon your point of view) statement that all of chemistry is reduced to physics by it:

> The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions . . . . The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble . . . .

To some, with what we might call a practical turn of mind, this seems silly. Our mathematical and computational abilities are not even close to being able to give useful general solutions to it. To those with a more philosophical outlook, it seems significant that, at our present level of understanding, Dirac's statement is apparently true. Therefore, progress made in methods of solving Eq. (1.4) is improving our ability at making predictions from this equation that are useful for answering chemical questions.

The Born–Oppenheimer approximation

In the early days of quantum mechanics Born and Oppenheimer[18] showed that the energy and motion of the nuclei and electrons could be separated approximately. This was accomplished using a perturbation treatment in which the perturbation parameter is $(m_e/M)^{1/4}$. In actuality, the term "Born–Oppenheimer approximation" is frequently ambiguous. It can refer to two somewhat different theories. The first is the reference above and the other one is found in an appendix of the book by Born and Huang on crystal structure[19]. In the latter treatment, it is assumed, based upon physical arguments, that the wave function of Eq. (1.4) may be written as the product of two other functions

$$\Psi(\vec{r}_i, \vec{r}_\alpha) = \phi(\vec{r}_\alpha)\psi(\vec{r}_i, \vec{r}_\alpha), \tag{1.5}$$

where the nuclear positions $\vec{r}_\alpha$ given in ψ are parameters rather than variables in the normal sense. The ϕ is the actual wave function for nuclear motion and will not concern us at all in this book. If Eq. (1.5) is substituted into Eq. (1.4), various terms are collected, and small quantities dropped, we obtain what is frequently called the Schrödinger equation for the electrons using the Born–Oppenheimer approximation

$$-\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2\psi + V\psi = E(\vec{r}_\alpha)\psi, \tag{1.6}$$

where we have explicitly observed the dependence of the energy on the nuclear positions by writing it as $E(\vec{r}_\alpha)$. Equation (1.6) might better be termed the Schrödinger equation for the electrons using the *adiabatic* approximation[20]. Of course, the only difference between this and Eq. (1.4) is the presence of the nuclear kinetic energy in the latter. A heuristic way of looking at Eq. (1.6) is to observe that it would arise if the masses of the nuclei all passed to infinity, i.e., the nuclei become stationary. Although a physically useful viewpoint, the actual validity of such a procedure requires some discussion, which we, however, do not give.

We now go farther, introducing atomic units and rearranging Eq. (1.6) slightly,

$$-\frac{1}{2}\sum_i \nabla_i^2\psi - \sum_{i\alpha}\frac{Z_\alpha}{r_{i\alpha}}\psi + \sum_{i<j}\frac{1}{r_{ij}}\psi + \sum_{\alpha<\beta}\frac{Z_\alpha Z_\beta}{r_{\alpha\beta}}\psi = E_e\psi. \tag{1.7}$$

This is the equation with which we must deal. We will refer to it so frequently, it will be convenient to have a brief name for it. It is the *electronic Schrödinger equation*, and we refer to it as the ESE. Solutions to it of varying accuracy have been calculated since the early days of quantum mechanics. Today, there exist computer programs both commercial and in the public domain that will carry out calculations to produce approximate solutions to the ESE. Indeed, a program of this sort is available from the author through the Internet.[3] Although not as large as some of the others available, it will do many of the things the bigger programs will do, as well as a couple of things they do not: in particular, this program will do VB calculations of the sort we discuss in this book.

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[3] The CRUNCH program, `http://phy-ggallup.unl.edu/crunch/`

1.3 The variation theorem

1.3.1 General variation functions

If we write the sum of the kinetic and potential energy operators as the Hamiltonian operator $T + V = H$, the ESE may be written as

$$H\Psi = E\Psi. \tag{1.8}$$

One of the remarkable results of quantum mechanics is the variation theorem, which states that

$$W = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} \geq E_0, \tag{1.9}$$

where E_0 is the lowest allowed eigenvalue for the system. The fraction in Eq. (1.9) is frequently called the *Rayleigh quotient*. The basic use of this result is quite simple. One uses arguments based on similarity, intuition, guess-work, or whatever, to devise a suitable function for Ψ. Using Eq. (1.9) then necessarily gives us an upper bound to the true lowest energy, and, if we have been clever or lucky, the upper bound is a good approximation to the lowest energy. The most common way we use this is to construct a trial function, Ψ, that has a number of parameters in it. The quantity, W, in Eq. (1.9) is then a function of these parameters, and a minimization of W with respect to the parameters gives the best result possible within the limitations of the choice for Ψ. We will use this scheme in a number of discussions throughout the book.

1.3.2 Linear variation functions

A trial variation function that has linear variation parameters only is an important special case, since it allows an analysis giving a systematic improvement on the lowest upper bound as well as upper bounds for excited states. We shall assume that $\phi_1, \phi_2, \ldots,$ represents a complete, normalized (but not necessarily orthogonal) set of functions for expanding the exact eigensolutions to the ESE. Thus we write

$$\Psi = \sum_{i=1}^{\infty} \phi_i C_i, \tag{1.10}$$

where the C_i are the variation parameters. Substituting into Eq. (1.9) we obtain

$$W = \frac{\sum_{ij} H_{ij} C_i^* C_j}{\sum_{ij} S_{ij} C_i^* C_j}, \tag{1.11}$$

where

$$H_{ij} = \langle\phi_i|H|\phi_j\rangle, \tag{1.12}$$

$$S_{ij} = \langle\phi_i|\phi_j\rangle. \tag{1.13}$$

We differentiate W with respect to the C_i^*s and set the results to zero to find the minimum, obtaining an equation for each C_i^*,

$$\sum_j (H_{ij} - WS_{ij})C_j = 0\,; \qquad i = 1, 2, \ldots. \tag{1.14}$$

In deriving this we have used the properties of the integrals $H_{ij} = H_{ji}^*$ and a similar result for S_{ij}. Equation (1.14) is discussed in all elementary textbooks wherein it is shown that a $C_j \neq 0$ solution exists only if the W has a specific set of values. It is sometimes called the *generalized eigenvalue problem* to distinguish from the case when S is the identity matrix. We wish to pursue further information about the Ws here.

Let us consider a variation function where we have chosen n of the functions, ϕ_i. We will then show that the eigenvalues of the n-function problem divide, i.e., occur between, the eigenvalues of the $(n+1)$-function problem. In making this analysis we use an extension of the methods given by Brillouin[21] and MacDonald[22].

Having chosen n of the ϕ functions to start, we obtain an equation like Eq. (1.14), but with only $n \times n$ matrices and n terms,

$$\sum_{j=1}^{n} \big(H_{ij} - W^{(n)}S_{ij}\big)C_j^{(n)} = 0\,; \qquad i = 1, 2, \ldots, n. \tag{1.15}$$

It is well known that sets of linear equations like Eq. (1.15) will possess nonzero solutions for the $C_j^{(n)}$s only if the matrix of coefficients has a rank less than n. This is another way of saying that the determinant of the matrix is zero, so we have

$$\big|H - W^{(n)}S\big| = 0. \tag{1.16}$$

When expanded out, the determinant is a polynomial of degree n in the variable $W^{(n)}$, and it has n real roots if H and S are both Hermitian matrices, and S is positive definite. Indeed, if S were not positive definite, this would signal that the basis functions were not all linearly independent, and that the basis was defective. If $W^{(n)}$ takes on one of the roots of Eq. (1.16) the matrix $H - W^{(n)}S$ is of rank $n-1$ or less, and its rows are linearly dependent. There is thus at least one more nonzero vector with components $C_j^{(n)}$ that can be orthogonal to all of the rows. This is the solution we want.

It is useful to give a matrix solution to this problem. We affix a superscript $^{(n)}$ to emphasize that we are discussing a matrix solution for n basis functions. Since $S^{(n)}$ is Hermitian, it may be diagonalized by a unitary matrix, $T = (T^\dagger)^{-1}$

$$T^\dagger S^{(n)} T = s^{(n)} = \mathrm{diag}\big(s_1^{(n)}, s_2^{(n)}, \ldots, s_n^{(n)}\big), \tag{1.17}$$

where the diagonal elements of $s^{(n)}$ are all real and positive, because of the Hermitian and positive definite character of the overlap matrix. We may construct the inverse square root of $s^{(n)}$, and, clearly, we obtain

$$\left[T\left(s^{(n)}\right)^{-1/2}\right]^{\dagger} S^{(n)} T\left(s^{(n)}\right)^{-1/2} = I. \tag{1.18}$$

We subject $H^{(n)}$ to the same transformation and obtain

$$\left[T\left(s^{(n)}\right)^{-1/2}\right]^{\dagger} H^{(n)} T\left(s^{(n)}\right)^{-1/2} = \bar{H}^{(n)}, \tag{1.19}$$

which is also Hermitian and may be diagonalized by a unitary matrix, U. Combining the various transformations, we obtain

$$V^{\dagger} H^{(n)} V = h^{(n)} = \mathrm{diag}\left(h_1^{(n)}, h_2^{(n)}, \ldots, h_n^{(n)}\right), \tag{1.20}$$

$$V^{\dagger} S^{(n)} V = I, \tag{1.21}$$

$$V = T\left(s^{(n)}\right)^{-1/2} U. \tag{1.22}$$

We may now combine these matrices to obtain the null matrix

$$V^{\dagger} H^{(n)} V - V^{\dagger} S^{(n)} V h^{(n)} = 0, \tag{1.23}$$

and multiplying this on the left by $(V^{\dagger})^{-1} = U(s^{(n)})^{1/2} T$ gives

$$H^{(n)} V - S^{(n)} V h^{(n)} = 0. \tag{1.24}$$

If we write out the k^{th} column of this last equation, we have

$$\sum_{j=1}^{n} \left(H_{ij}^{(n)} - h_k^{(n)} S_{ij}^{(n)}\right) V_{jk} = 0; \qquad i = 1, 2, \ldots, n. \tag{1.25}$$

When this is compared with Eq. (1.15) we see that we have solved our problem, if $C^{(n)}$ is the k^{th} column of V and $W^{(n)}$ is the k^{th} diagonal element of $h^{(n)}$. Thus the diagonal elements of $h^{(n)}$ are the roots of the determinantal equation Eq. (1.16).

Now consider the variation problem with $n + 1$ functions where we have added another of the basis functions to the set. We now have the matrices $H^{(n+1)}$ and $S^{(n+1)}$, and the new determinantal equation

$$\left|H^{(n+1)} - W^{(n+1)} S^{(n+1)}\right| = 0. \tag{1.26}$$

We may subject this to a transformation by the $(n + 1) \times (n + 1)$ matrix

$$\bar{V} = \begin{bmatrix} V & 0 \\ 0 & 1 \end{bmatrix}, \tag{1.27}$$

and $H^{(n+1)}$ and $S^{(n+1)}$ are modified to

$$\bar{V}^{\dagger} H^{(n+1)} \bar{V} = \bar{H}^{(n+1)} = \begin{bmatrix} h_1^{(n)} & 0 & \cdots & \bar{H}^{(n+1)}_{1\,n+1} \\ 0 & h_2^{(n)} & \cdots & \bar{H}^{(n+1)}_{2\,n+1} \\ \vdots & \vdots & \ddots & \vdots \\ \bar{H}^{(n+1)}_{n+1\,1} & \bar{H}^{(n+1)}_{n+1\,2} & \cdots & H^{n+1}_{n+1\,n+1} \end{bmatrix} \tag{1.28}$$

and

$$\bar{V}^{\dagger} S^{(n+1)} \bar{V} = \bar{S}^{(n+1)} = \begin{bmatrix} 1 & 0 & \cdots & \bar{S}^{(n+1)}_{1\,n+1} \\ 0 & 1 & \cdots & \bar{S}^{(n+1)}_{2\,n+1} \\ \vdots & \vdots & \ddots & \vdots \\ \bar{S}^{(n+1)}_{n+1\,1} & \bar{S}^{(n+1)}_{n+1\,2} & \cdots & 1 \end{bmatrix}. \tag{1.29}$$

Thus Eq. (1.26) becomes

$$0 = \begin{vmatrix} h_1^{(n)} - W^{(n+1)} & 0 & \cdots & \bar{H}^{(n+1)}_{1\,n+1} - W^{(n+1)} \bar{S}^{(n+1)}_{1\,n+1} \\ 0 & h_2^{(n)} - W^{(n+1)} & \cdots & \bar{H}^{(n+1)}_{2\,n+1} - W^{(n+1)} \bar{S}^{(n+1)}_{2\,n+1} \\ \vdots & \vdots & \ddots & \vdots \\ \bar{H}^{(n+1)}_{n+1\,1} - W^{(n+1)} \bar{S}^{(n+1)}_{n+1\,1} & \bar{H}^{(n+1)}_{n+1\,2} - W^{(n+1)} \bar{S}^{(n+1)}_{n+1\,2} & \cdots & H^{n+1}_{n+1\,n+1} - W^{(n+1)} \end{vmatrix}. \tag{1.30}$$

We modify the determinant in Eq. (1.30) by using column operations. Multiply the i^{th} column by

$$\frac{\bar{H}^{(n+1)}_{i\,n+1} - W^{(n+1)} \bar{S}^{(n+1)}_{i\,n+1}}{h_i^{(n)} - W^{(n+1)}}$$

and subtract it from the $(n+1)^{\text{th}}$ column. This is seen to cancel the i^{th} row element in the last column. Performing this action for each of the first n columns, the determinant is converted to lower triangular form, and its value is just the product of the diagonal elements,

$$\begin{aligned} 0 &= D^{(n+1)}\big(W^{(n+1)}\big) \\ &= \prod_{i=1}^{n} \left[h_i^{(n)} - W^{(n+1)}\right] \\ &\quad \times \left[\bar{H}^{(n)}_{n+1\,n+1} - W^{(n+1)} - \sum_{i=1}^{n} \frac{\left|\bar{H}^{(n+1)}_{i\,n+1} - W^{(n+1)} \bar{S}^{(n+1)}_{i\,n+1}\right|^2}{h_i^{(n)} - W^{(n+1)}} \right]. \end{aligned} \tag{1.31}$$

Examination shows that $D^{(n+1)}(W^{(n+1)})$ is a polynomial in $W^{(n+1)}$ of degree $n+1$, as it should be.

We note that none of the $h_i^{(n)}$ are normally roots of $D^{(n+1)}$,

$$\lim_{W^{(n+1)}\to h_i^{(n)}} D^{(n+1)} = \prod_{j\neq i}\left[h_j^{(n)} - h_i^{(n)}\right]\left|\bar{H}_{i\,n+1}^{(n+1)} - h_i^{(n)}\bar{S}_{i\,n+1}^{(n+1)}\right|^2, \tag{1.32}$$

and would be only if the $h_i^{(n)}$ were degenerate or the second factor $|\cdots|^2$ were zero.[4]

Thus, $D^{(n+1)}$ is zero when the second $[\cdots]$ factor of Eq. (1.31) is zero,

$$\bar{H}_{n+1\,n+1}^{(n+1)} - W^{(n+1)} = \sum_{i=1}^{n} \frac{\left|\bar{H}_{i\,n+1}^{(n+1)} - W^{(n+1)}\bar{S}_{i\,n+1}^{(n+1)}\right|^2}{h_i^{(n)} - W^{(n+1)}}. \tag{1.33}$$

It is most useful to consider the solution of Eq. (1.33) graphically by plotting both the right and left hand sides versus $W^{(n+1)}$ on the same graph and determining where the two curves cross. For this purpose let us suppose that $n = 4$, and we consider the right hand side. It will have poles on the real axis at each of the $h_i^{(4)}$. When $W^{(5)}$ becomes large in either the positive or negative direction the right hand side asymptotically approaches the line

$$y = \sum_{i=1}^{4}\left(\bar{H}_{i\,5}^{*}\bar{S}_{i\,5} + \bar{H}_{i\,5}\bar{S}_{i\,5}^{*} - W^{(5)}\left|\bar{S}_{i\,5}^{(5)}\right|^2\right).$$

It is easily seen that the determinant of $\bar{S}$ is

$$|\bar{S}| = 1 - \sum_{i=1}^{4}\left|\bar{S}_{i\,5}^{(5)}\right|^2 > 0, \tag{1.34}$$

and, if equal to zero, S would not be positive definite, a circumstance that would happen only if our basis were linearly dependent. Thus, the asymptotic line of the right hand side has a slope between 0 and –45°. We see this in Fig. 1.1. The left hand side of Eq. (1.33) is, on the other hand, just a straight line of exactly –45° slope and a $W^{(5)}$ intercept of $\bar{H}_{5\,5}^{(5)}$. This is also shown in Fig. 1.1. The important point we note is that the right hand side of Eq. (1.33) has five branches that intersect the left hand line in five places, and we thus obtain five roots. The vertical dotted lines in Fig. 1.1 are the values of the $h_i^{(4)}$, and we see there is one of these between each pair of roots for the five-function problem. A little reflection will indicate that this important fact is true for any n, not just the special case plotted in Fig. 1.1.

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[4] We shall suppose neither of these possibilities occurs, and in practice neither is likely in the absence of symmetry. If there is symmetry present that can produce degeneracy or zero factors of the $[\cdots]^2$ sort, we assume that symmetry factorization has been applied and that all functions we are working with are within one of the closed symmetry subspaces of the problem.

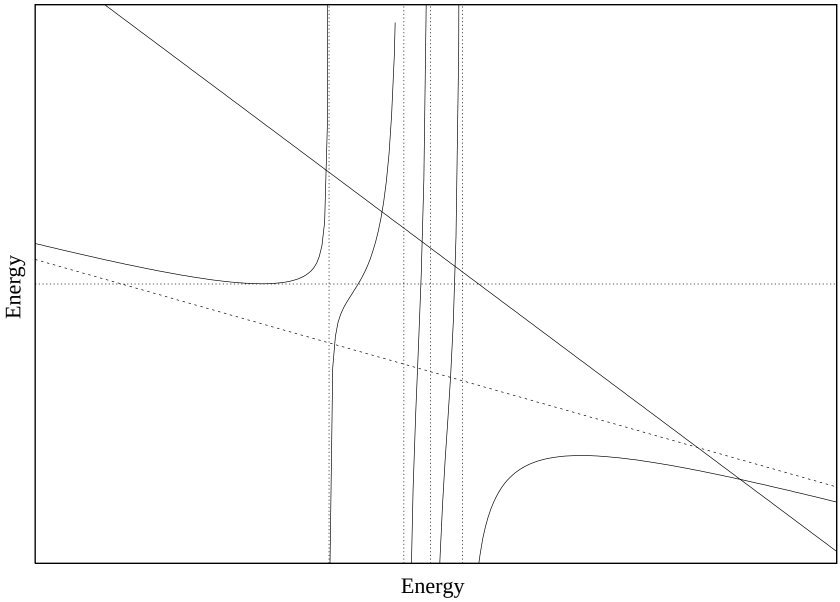

Figure 1.1. The relationship between the roots for $n = 4$ (the abscissa intercepts of the vertical dotted lines) and $n = 5$ (abscissas of intersections of solid lines with solid curves) shown graphically.

The upshot of these considerations is that a series of matrix solutions of the variation problem, where we add one new function at a time to the basis, will result in a series of eigenvalues in a pattern similar to that shown schematically in Fig. 1.2, and that the order of adding the functions is immaterial. Since we suppose that our ultimate basis ($n \to \infty$) is complete, each of the eigenvalues will become exact as we pass to an infinite basis, and we see that the sequence of n-basis solutions converges to the correct answer from above. The rate of convergence at various levels will certainly depend upon the order in which the basis functions are added, but not the ultimate value.

1.3.3 A 2 × 2 generalized eigenvalue problem

The generalized eigenvalue problem is unfortunately considerably more complicated than its regular counterpart when $S = I$. There are possibilities for accidental cases when basis functions apparently should mix, but they do not. We can give a simple example of this for a 2×2 system. Assume we have the pair of matrices

$$H = \begin{bmatrix} A & B \\ B & C \end{bmatrix} \tag{1.35}$$

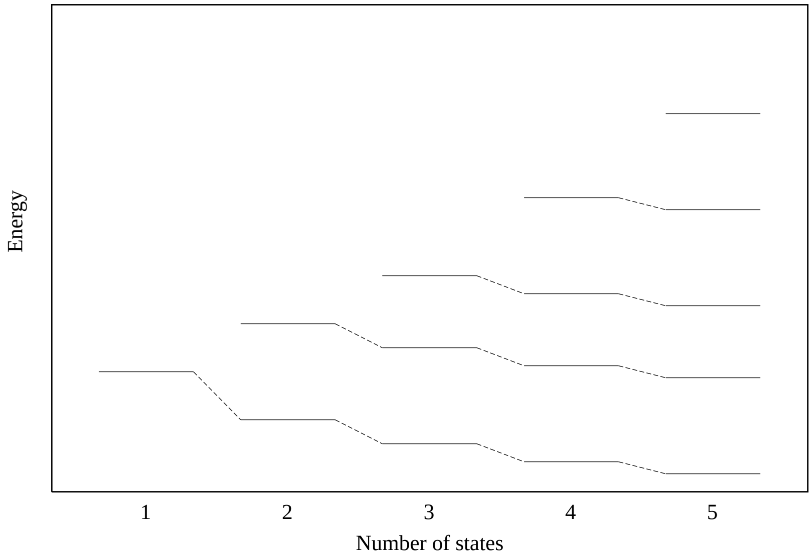

Figure 1.2. A qualitative graph showing schematically the interleaving of the eigenvalues for a series of linear variation problems for $n = 1, \ldots, 5$. The ordinate is energy.

and

$$S = \begin{bmatrix} 1 & s \\ s & 1 \end{bmatrix}, \tag{1.36}$$

where we assume for the argument that $s > 0$. We form the matrix H'

$$\begin{aligned} H' &= H - \frac{A+C}{2} S, \\ &= \begin{bmatrix} a & b \\ b & -a \end{bmatrix}, \end{aligned} \tag{1.37}$$

where

$$a = A - \frac{A+C}{2} \tag{1.38}$$

and

$$b = B - \frac{A+C}{2} s. \tag{1.39}$$

It is not difficult to show that the eigenvectors of H' are the same as those of H.

Our generalized eigenvalue problem thus depends upon three parameters, a, b, and s. Denoting the eigenvalue by W and solving the quadratic equation, we obtain

$$W = -\frac{sb}{(1-s^2)} \pm \frac{\sqrt{a^2(1-s^2)+b^2}}{(1-s^2)}. \tag{1.40}$$

We note the possibility of an accident that cannot happen if $s = 0$ and $b \neq 0$: Should $b = \pm as$, one of the two values of W is either $\pm a$, and one of the two diagonal elements of H' is unchanged.[5] Let us for definiteness assume that $b = as$ and it is a we obtain. Then, clearly the vector C_1 we obtain is

$$\begin{bmatrix} 1 \\ 0 \end{bmatrix},$$

and there is no mixing between the states from the application of the variation theorem. The other eigenvector is simply determined because it must be orthogonal to C_1, and we obtain

$$C_2 = \begin{bmatrix} -s/\sqrt{1-s^2} \\ 1/\sqrt{1-s^2} \end{bmatrix},$$

so the other state is mixed. It must normally be assumed that this accident is rare in practical calculations. Solving the generalized eigenvalue problem results in a nonorthogonal basis changing both directions and internal angles to become orthogonal. Thus one basis function could get “stuck” in the process. This should be contrasted with the case when $S = I$, in which basis functions are unchanged only if the matrix was originally already diagonal with respect to them.

We do not discuss it, but there is an $n \times n$ version of this complication. If there is no degeneracy, one of the diagonal elements of the H-matrix may be unchanged in going to the eigenvalues, and the eigenvector associated with it is $[0, \dots, 0, 1, 0, \dots, 0]^\dagger$.

1.4 Weights of nonorthogonal functions

The probability interpretation of the wave function in quantum mechanics obtained by forming the square of its magnitude leads naturally to a simple idea for the weights of constituent parts of the wave function when it is written as a linear combination of orthonormal functions. Thus, if

$$\Psi = \sum_i \psi_i C_i, \tag{1.41}$$

and $\langle \psi_i | \psi_j \rangle = \delta_{ij}$, normalization of Ψ requires

$$\sum_i |C_i|^2 = 1. \tag{1.42}$$

If, also, each of the ψ_i has a certain physical interpretation or significance, then one says the wave function Ψ, or the state represented by it, consists of a fraction

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[5] NB We assumed this not to happen in our discussion above of the convergence in the linear variation problem.

$|C_i|^2$ of the state represented by ψ_i. One also says that the *weight*, w_i of ψ_i in Ψ is $w_i = |C_i|^2$.

No such simple result is available for nonorthogonal bases, such as our VB functions, because, although they are normalized, they are not mutually orthogonal. Thus, instead of Eq. (1.42), we would have

$$\sum_{ij} C_i^* C_j S_{ij} = 1, \tag{1.43}$$

if the ψ_i were not orthonormal. In fact, at first glance orthogonalizing them would mix together characteristics that one might wish to consider separately in determining weights. In the author's opinion, there has not yet been devised a completely satisfactory solution to this problem. In the following paragraphs we mention some suggestions that have been made and, in addition, present yet another way of attempting to resolve this problem.

In Section 2.8 we discuss some simple functions used to represent the H_2 molecule. We choose one involving six basis functions to illustrate the various methods. The overlap matrix for the basis is

$$\begin{bmatrix} 1.000\,000 & & & & & \\ 0.962\,004 & 1.000\,000 & & & & \\ 0.137\,187 & 0.181\,541 & 1.000\,000 & & & \\ -0.254\,383 & -0.336\,628 & 0.141\,789 & 1.000\,000 & & \\ 0.181\,541 & 0.137\,187 & 0.925\,640 & 0.251\,156 & 1.000\,000 & \\ 0.336\,628 & 0.254\,383 & -0.251\,156 & -0.788\,501 & -0.141\,789 & 1.000\,000 \end{bmatrix},$$

and the eigenvector we analyze is

$$\begin{bmatrix} 0.283\,129 \\ 0.711\,721 \\ 0.013\,795 \\ -0.038\,111 \\ -0.233\,374 \\ 0.017\,825 \end{bmatrix}. \tag{1.44}$$

S is to be filled out, of course, so that it is symmetric. The particular chemical or physical significance of the basis functions need not concern us here.

The methods below giving sets of weights fall into one of two classes: those that involve no orthogonalization and those that do. We take up the former group first.

Table 1.1. *Weights for nonorthogonal basis functions by various methods.*

Chirgwin–Coulson	Inverse-overlap	Symmetric orthogon.	EGSO[a]
0.266 999	0.106 151	0.501 707	0.004 998
0.691 753	0.670 769	0.508 663	0.944 675
–0.000 607	0.000 741	0.002 520	0.000 007
0.016 022	0.008 327	0.042 909	0.002 316
0.019 525	0.212 190	0.051 580	0.047 994
0.006 307	0.001 822	0.000 065	0.000 010

[a] EGSO = eigenvector guided sequential orthogonalization.

1.4.1 *Weights without orthogonalization*

The method of Chirgwin and Coulson

These workers[23] suggest that one use

$$w_i = C_i^* \sum_j S_{ij} C_j, \tag{1.45}$$

although, admittedly, they proposed it only in cases where the quantities were real. As written, this w_i is not guaranteed even to be real, and when the C_i and S_{ij} are real, it is not guaranteed to be positive. Nevertheless, in simple cases it can give some idea for weights. We show the results of applying this method to the eigenvector and overlap matrix in Table 1.1 above. We see that the relative weights of basis functions 2 and 1 are fairly large and the others are quite small.

Inverse overlap weights

Norbeck and the author[24] suggested that in cases where there is overlap, the basis functions each can be considered to have a unique portion. The “length” of this may be shown to be equal to the reciprocal of the diagonal of the S^{-1} matrix corresponding to the basis function in question. Thus, if a basis function has a unique portion of very short length, a large coefficient for it means little. This suggests that a set of *relative* weights could be obtained from

$$w_i \propto |C_i|^2/(S^{-1})_{ii}, \tag{1.46}$$

where these w_i do not generally sum to 1. As implemented, these weights are renormalized so that they do sum to 1 to provide convenient fractions or percentages. This is an awkward feature of this method and makes it behave nonlinearly in some contexts. Although these first two methods agree as to the most important basis function they transpose the next two in importance.

1.4.2 Weights requiring orthogonalization

We emphasize that here we are speaking of orthogonalizing the VB basis not the underlying atomic orbitals (AOs). This can be accomplished by a transformation of the overlap matrix to convert it to the identity

$$N^{\dagger} S N = I. \tag{1.47}$$

Investigation shows that N is far from unique. Indeed, if N satisfies Eq. (1.47), NU will also work, where U is any unitary matrix. A possible candidate for N is shown in Eq. (1.18). If we put restrictions on N, the result can be made unique. If N is forced to be upper triangular, one obtains the classical *Schmidt orthogonalization* of the basis. The transformation of Eq. (1.18), as it stands, is frequently called the *canonical orthogonalization* of the basis. Once the basis is orthogonalized the weights are easily determined in the normal sense as

$$w_i = \left| \sum_j (N^{-1})_{ij} C_j \right|^2, \tag{1.48}$$

and, of course, they sum to 1 exactly without modification.

Symmetric orthogonalization

Löwdin[25] suggested that one find the orthonormal set of functions that most closely approximates the original nonorthogonal set in the least squares sense and use these to determine the weights of various basis functions. An analysis shows that the appropriate transformation in the notation of Eq. (1.18) is

$$N = T\left(s^{(n)}\right)^{-1/2} T^{\dagger} = S^{-1/2} = (S^{-1/2})^{\dagger}, \tag{1.49}$$

which is seen to be the inverse of one of the square roots of the overlap matrix and Hermitian (symmetric, if real). Because of this symmetry, using the N of Eq. (1.49) is frequently called a *symmetric orthogonalization*. This translates easily into the set of weights

$$w_i = \left| \sum_j (S^{1/2})_{ij} C_j \right|^2, \tag{1.50}$$

which sums to 1 without modification. These are also shown in Table 1.1. We now see weights that are considerably different from those in the first two columns. w_1 and w_2 are nearly equal, with w_2 only slightly larger. This is a direct result of the relatively large value of S_{12} in the overlap matrix, but, indirectly, we note that the hypothesis behind the symmetric orthogonalization can be faulty. A least squares problem like that resulting in this orthogonalization method, in principle, always has an answer, but that gives no guarantee at all that the functions produced really are close to the original ones. That is really the basic difficulty. Only if the overlap matrix were, in some sense, close to the identity would this method be expected to yield useful results.

An eigenvector guided sequential orthogonalization (EGSO)

As promised, with this book we introduce another suggestion for determining weights in VB functions. Let us go back to one of the ideas behind inverse overlap weights and apply it differently. The existence of nonzero overlaps between different basis functions suggests that some "parts" of basis functions are duplicated in the sum making up the total wave function. At the same time, consider function 2 (the second entry in the eigenvector (1.44)). The eigenvector was determined using linear variation functions, and clearly, there is something about function 2 that the variation theorem likes, it has the largest (in magnitude) coefficient. Therefore, we take all of that function in our orthogonalization, and, using a procedure analogous to the Schmidt procedure, orthogonalize all of the remaining functions of the basis to it. This produces a new set of Cs, and we can carry out the process again with the largest remaining coefficient. We thus have a stepwise procedure to orthogonalize the basis. Except for the order of choice of functions, this is just a Schmidt orthogonalization, which normally, however, involves an arbitrary or preset ordering.

Comparing these weights to the others in Table 1.1 we note that there is now one truly dominant weight and the others are quite small. Function 2 is really a considerable portion of the total function at 94.5%. Of the remaining, only function 5 at 4.8% has any size. It is interesting that the two methods using somewhat the same idea predict the same two functions to be dominant.

If we apply this procedure to a different state, there will be a different ordering, in general, but this is expected. The orthogonalization in this procedure is not designed to generate a basis for general use, but is merely a device to separate characteristics of basis functions into noninteracting pieces that allows us to determine a set of weights. Different eigenvalues, i.e., different states, may well be quite different in this regard.

We now outline the procedure in more detail. Deferring the question of ordering until later, let us assume we have found an upper triangular transformation matrix, N_k, that converts S as follows:

$$(N_k)^\dagger S N_k = \begin{bmatrix} I_k & 0 \\ 0 & S_{n-k} \end{bmatrix}, \tag{1.51}$$

where I_k is a $k \times k$ identity, and we have determined k of the orthogonalized weights. We show how to determine N_{k+1} from N_k.

Working only with the lower right $(n-k) \times (n-k)$ corner of the matrices, we observe that S_{n-k} in Eq. (1.51) is just the overlap matrix for the unreduced portion of the basis and is, in particular, Hermitian, positive definite, and with diagonal elements equal to 1. We write it in partitioned form as

$$S_{n-k} = \begin{bmatrix} 1 & s \\ s^\dagger & S' \end{bmatrix}, \tag{1.52}$$

where $[1 \quad s]$ is the first row of the matrix. Let M_{n-k} be an upper triangular matrix partitioned similarly,

$$M_{n-k} = \begin{bmatrix} 1 & q \\ 0 & B \end{bmatrix}, \tag{1.53}$$

and we determine q and B so that

$$(M_{n-k})^\dagger S_{n-k} M_{n-k} = \begin{bmatrix} 1 & q + sB \\ (q + sB)^\dagger & B^\dagger(S' - s^\dagger s)B \end{bmatrix}, \tag{1.54}$$

$$= \begin{bmatrix} 1 & 0 \\ 0 & S_{n-k-1} \end{bmatrix}, \tag{1.55}$$

where these equations may be satisfied with B the diagonal matrix

$$B = \operatorname{diag}\Big(\big(1 - s_1^2\big)^{-1/2} \, \big(1 - s_2^2\big)^{-1/2} \cdots\Big) \tag{1.56}$$

and

$$q = -sB. \tag{1.57}$$

The inverse of M_{n-k} is easily determined:

$$(M_{n-k})^{-1} = \begin{bmatrix} 1 & s \\ 0 & B^{-1} \end{bmatrix}, \tag{1.58}$$

and, thus, $N_{k+1} = N_k Q_k$, where

$$Q_k = \begin{bmatrix} I_k & 0 \\ 0 & M_{n-k} \end{bmatrix}. \tag{1.59}$$

The unreduced portion of the problem is now transformed as follows:

$$(C_{n-k})^\dagger S_{n-k} C_{n-k} = [(M_{n-k})^{-1} C_{n-k}]^\dagger (M_{n-k})^\dagger S_{n-k} M_{n-k} [(M_{n-k})^{-1} C_{n-k}]. \tag{1.60}$$

Writing

$$C_{n-k} = \begin{bmatrix} C_1 \\ C' \end{bmatrix}, \tag{1.61}$$

we have

$$[(M_{n-k})^{-1} C_{n-k}] = \begin{bmatrix} C_1 + sC' \\ B^{-1}C' \end{bmatrix}, \tag{1.62}$$

$$= \begin{bmatrix} C_1 + sC' \\ C_{n-k-1} \end{bmatrix}. \tag{1.63}$$

Putting these together, we arrive at the total N as $Q_1 Q_2 Q_3 \cdots Q_{n-1}$.

What we have done so far is, of course, no different from a standard top-down Schmidt orthogonalization. We wish, however, to guide the ordering with the eigenvector. This we accomplish by inserting before each Q_k a binary permutation matrix P_k that puts in the top position the $C_1 + sC'$ from Eq. (1.63) that is largest in magnitude. Our actual transformation matrix is

$$N = P_1 Q_1 P_2 Q_2 \cdots P_{n-1} Q_{n-1}. \tag{1.64}$$

Then the weights are simply as given (for basis functions in a different order) by Eq. (1.48). We observe that choosing $C_1 + sC'$ as the test quantity whose magnitude is maximized is the same as choosing the remaining basis function from the unreduced set that at each stage gives the greatest contribution to the total wave function.

There are situations in which we would need to modify this procedure for the results to make sense. Where symmetry dictates that two or more basis functions should have equal contributions, the above algorithm could destroy this equality. In these cases some modification of the procedure is required, but we do not need this extension for the applications of the EGSO weights found in this book.