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Experiments in Quantum Chemistry: The Linear Variation Method

For most problems in quantum chemistry the Hamiltonian operator describing the system is easy to write down. The difficulty is that the resulting Schroedinger equation usually cannot be solved analytically. Fortunately, with digital computers, useful approximate energy levels and wavefunctions may be obtained using numerical methods. The wide availability of computers has expanded enormously the usefulness of quantum mechanics for the chemist and even elementary courses in quantum chemistry and molecular spectroscopy often include their use.

Unfortunately elaborate computer programs like complex pieces of laboratory apparatus can appear to the student like mysterious black boxes which deliver answers with little meaning or educational value. In this paper we will show how a single simple computer program can be used to study a multitude of problems in quantum chemistry. These problems include doing Hückel molecular-orbital calculations, determining energy levels and wavefunctions for the anharmonic oscillator, the hindered rotor, and the perturbed particle in a box, calculating the ground state energy of the helium atom, analyzing magnetic resonance spectra, and so on. The technique used in the calculations we will discuss is the linear variation method. A computer program solves the secular equations to provide eigenvalues and eigenfunctions.

Experiment in the dictionary entry is, in part, "to demonstrate some known truth" (1). In keeping with this definition, we have labeled our calculations "experiments." Our examples allow for a wide variety of input data choices and the results either demonstrate theorems of quantum chemistry or may be compared directly to laboratory measurements. The computer, like the spectrometer or analytical balance, is therefore just another experimental tool which when used with care can demonstrate chemical principles.

Theory

The presentation of the linear variation technique appears in most quantum chemistry textbooks (2-7). The problem is to determine approximate solutions to the Schroedinger equation,

$$\hat{H}\psi_i = E_i\psi_i \quad (1)$$

for which neither the true eigenfunctions, ψ_i , nor true eigenvalues or energies, E_i , are known. In the linear variation method we approximate the true eigenfunction by a trial function which is a linear combination of n linearly independent functions,

$$\psi \approx \phi = c_1f_1 + c_2f_2 + \dots + c_nf_n = \sum_{j=1}^n c_j f_j \quad (2)$$

The basis functions, f_j , must be well behaved and satisfy the boundary conditions of the problem.

The energy associated with the trial function is given by the variational integral,

¹Present address: Mont Alto Campus, Pennsylvania State University, Mont Alto, Pennsylvania 17237.

²The program is available from the authors upon request. It requires two subroutines, QCPE program numbers 62.4 and 97, which are available from the Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Indiana 47401. A listing and punched cards may be obtained for \$98.50. The fee is waived in hardship cases.

$$W(c_1, c_2, \dots, c_n) = \frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau} = \frac{\sum_{j=1}^n \sum_{k=1}^n c_j c_k H_{jk}}{\sum_{j=1}^n \sum_{k=1}^n c_j c_k S_{jk}} \quad (3)$$

where

$$H_{jk} = \int f_j^* \hat{H} f_k d\tau \quad (4)$$

and

$$S_{jk} = \int f_j^* f_k d\tau \quad (5)$$

Now the variation theorem assures us that for any choice of the c_j coefficients the approximate energy will be greater than the true lowest energy value of \hat{H} ,

$$W \geq E_o$$

We must therefore systematically adjust all the c_j coefficients to minimize W in order to get as good an approximation as possible to the true energy. This is accomplished by the condition $\partial W / \partial c_i = 0$ for $i = 1, 2, \dots, n$ and leads to the set of equations

$$\sum_{k=1}^n [(H_{ik} - S_{ik} W) c_k] = 0 \quad i = 1, 2, \dots, n \quad (6)$$

These equations have solutions of physical significance only if the secular determinant is zero,

$$\begin{vmatrix} H_{11} - S_{11} W & H_{12} - S_{12} W & \dots & H_{1n} - S_{1n} W \\ H_{21} - S_{21} W & H_{22} - S_{22} W & \dots & H_{2n} - S_{2n} W \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1} - S_{n1} W & H_{n2} - S_{n2} W & \dots & H_{nn} - S_{nn} W \end{vmatrix} = 0 \quad (7)$$

The n roots, W_0, W_1, \dots, W_{n-1} to this secular determinant are approximations to the exact energies of the original Schroedinger equation. From MacDonald's theorem (6) these energies (when arranged in order of increasing values) provide upper bounds to the true energies of eqn. (1).

$$E_o \leq W_0, E_1 \leq W_1, \dots, E_{n-1} \leq W_{n-1} \quad (8)$$

By taking enough terms in the expansion of eqn. (2), the energies W_i can be made to approximate the true energies E_i to a high degree of accuracy—in some cases one part in 10^{12} (12).

Any one of the roots W_i when substituted into eqn. (6) will generate a set of c_j coefficients which then specifies the approximate eigenfunction, $\psi_i \approx \phi_i$, of eqn. (1).

We, therefore, have a recipe for obtaining solutions to the original Schroedinger equation. We need only select the functions f_j and produce the matrix elements S_{ij} and H_{ij} . The computer program in solving eqn. (6) and (7) can then generate the approximate eigenfunctions and eigenvalues.

The Computer Technique

Our program, which is put together from subroutines available from the Quantum Chemistry Program Exchange,² is run on the CDC 6600 computer and sample run times are a fraction of a second for 10 term trial variation functions. Since the entire program is in FORTRAN IV, it can be implemented easily on most college and university computers.

Some Experiments

The Anharmonic Oscillator

The harmonic oscillator is an example treated in all elementary quantum chemistry texts (2-7). The Hamiltonian operator for the problem

$$\hat{H} = -\frac{\hbar^2 d^2}{2\mu dx^2} + \frac{1}{2}kx^2 \quad (9)$$

is expressed in terms of a mass μ which can be displaced by a distance x against a force constant k . The potential energy term for the problem, $\frac{1}{2}kx^2$, is quadratic in the displacement. The harmonic oscillator wavefunctions, ψ_ν , which are solutions of eqn. (9) are well known. The low lying energy levels of the harmonic oscillator reproduce the observed vibrational spacings of the stretching modes of most molecules usually with an accuracy better than 1%. For a more accurate description of the potential energy, cubic, quartic, and higher terms in the displacement must be included to yield a more complicated Hamiltonian,

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2}kx^2 + cx^3 + dx^4 + \dots \quad (10)$$

Analytical solutions of the anharmonic oscillator are not available. If the anharmonic terms, cx^3 and dx^4 , are small relative to the quadratic term, $\frac{1}{2}kx^2$, then perturbation treatments will yield energy levels to a reasonable degree of approximation. However an accurate calculation of the energy levels of the anharmonic oscillator may be obtained by the linear variation method no matter how large the cubic, quartic or higher order terms are.

In our example let us determine the energy levels of the quartic oscillator whose Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + dx^4 \quad (11)$$

The quartic oscillator is actually a reasonable description of bending modes and out-of-plane deformations of a number of molecules (9).

The trial functions for the quartic oscillator are written as an expansion of harmonic oscillator functions (the eigenfunctions of eqn. (9)),

$$\phi = c_0\psi_0 + c_1\psi_1 + \dots + c_\nu\psi_\nu \quad (12)$$

The evaluation of the overlap integrals follows from the orthonormal properties of the harmonic oscillator wavefunctions

$$S_{\nu\nu'} = \int \psi_\nu \psi_{\nu'} d\tau = \delta_{\nu\nu'} \quad (13)$$

The energy matrix elements of the kinetic and potential energy terms of eqn. (11) may be obtained by use of recursion relationships or from listings in various sources (9-11). The only non-zero matrix elements are found to be, in units of $(d\hbar^2/32\mu^2)^{1/3}$,

$$H_{\nu,\nu} = (3\nu^2 + 5\nu + 5/2)$$

$$H_{\nu,\nu-2} = 2(\nu - 1)\sqrt{\nu(\nu - 1)} \\ H_{\nu,\nu-4} = \frac{1}{2}\sqrt{\nu(\nu - 1)(\nu - 2)(\nu - 3)} \quad (14)$$

The energy levels generated for expansions of the trial function into 1, 3, or 5 harmonic oscillator wave functions are shown in Figure 1. The "exact" energies of the quartic oscillator were obtained by Tipping (12) using the linear variation method with a basis set of 100 functions and are believed to be accurate to 12 significant figures. The ordering of the calculated energy levels for different sizes of basis sets illustrates MacDonald's theorem stated by eqn. (8). In all cases $W_i \geq E_i$. The low lying levels require a smaller basis set to yield accurate energies than do the upper levels.

Our energy levels can of course be improved by extending the expansion beyond 5 functions. If we decide to use 10 harmonic oscillator

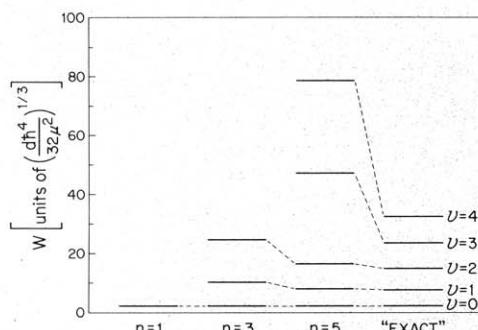


Figure 1. The energy levels of a quartic oscillator. The trial wavefunction is approximated by $n = 1, 3$, or 5 harmonic oscillator wavefunctions to obtain approximate energy levels. The "exact" energy levels which uses a basis set of 100 functions were taken from Ref. (12).

functions $\phi = c_1f_1 + c_2f_2 + \dots + c_{10}f_{10}$ with $f_1, f_2, \dots, f_{10} = \psi_0, \psi_1, \dots, \psi_9$ to obtain W_0, W_1, \dots, W_9 energies we could solve a 10×10 determinant. The form of this secular determinant is shown in Figure 2a where the cross-hatched sections indicate non-zero, $H_{\nu\nu'} - S_{\nu\nu'}W$, matrix elements. The pattern results because of eqn. (14) which states that only changes in ν by $0, \pm 2$ or ± 4 result in non zero $H_{\nu\nu'}$ elements. The checkered nature of the pattern illustrates the selection rule for our problem which states that a zero matrix element, $H_{\nu\nu'} - S_{\nu\nu'}W$, will result whenever ν is odd and ν' is even or vice-versa. We can take advantage of this fact to arrange the basis functions by even and odd quantum numbers to form a new expansion,

$$\phi' = c'_1f'_1 + c'_2f'_2 + \dots + c'_{10}f'_{10}$$

with $f'_1, f'_2, f'_3, f'_4, f'_5 = \psi_0, \psi_2, \psi_4, \psi_6, \psi_8$
and $f'_6, f'_7, f'_8, f'_9, f'_{10} = \psi_1, \psi_3, \psi_5, \psi_7, \psi_9$

The form of the resulting determinant is said to be block diagonal and is illustrated in Figure 2b. Grouping basis functions according to symmetry is a useful technique in quantum chemistry. In our example the procedure does not save time in generating matrix elements, but it does save computer time since two 5×5 determinants are quicker to solve than one 10×10 determinant.

A variety of computer experiments can be performed with the anharmonic oscillator. The mixed quadratic-quartic oscillator can be used to fit spectroscopic data for observed vibrational frequencies. The quadratic-cubic-quartic terms can be used to understand the anharmonicity of the vibration of a diatomic molecule. These results can be compared to textbook examples using perturbation theory. The vibrational motion of hydrogen in a hydrogen bonded molecule A-H...B may be described (10). The properties of the sextic oscillator may be investigated. Fortunately the matrix elements for all these suggested problems have been derived (10-11).

The Perturbed Particle in a Box

Another example treated in quantum chemistry texts is the particle-in-a-box. The Hamiltonian for the problem,

$$\hat{H}^0 = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} \quad (15)$$

is expressed in terms of a particle of mass m moving inside a one dimensional box defined by $V = 0$ in a certain region and $V = \infty$ outside this region. Choosing the box to be of length l with $V = \infty$ at $x = 0$ and $x = l$, leads to the familiar particle-in-the box eigenfunctions

$$\psi_n^0 = \left(\frac{2}{l}\right)^{1/2} \sin \frac{n\pi x}{l} \quad (16)$$

with energies given by

$$E_n^0 = \frac{n^2\pi^2\hbar^2}{2ml^2} \quad (17)$$

The particle-in-the box is the basis of perhaps the simplest semi-empirical pi-electron theory, the free-electron molecular-orbital (FEMO) model (13). In the FEMO treatment of a conjugated linear molecule the π -electrons are thought of as being noninteracting and confined to a one-dimensional box coincident with the molecular axis. This model has been found to be surprisingly successful in correlating and interpreting the spectra of conjugated linear molecules.

In our example let us apply the FEMO model to octatetraene, assuming that the π -electrons move in the constant potential of a particle-in-a-box. The choice of box length is taken to be $l = 1.4N_c$ where N_c is the number of C atoms (in this case $N_c = 8$) and 1.4 \AA is the average of C-C and C=C bond lengths. The lowest five energy levels for this crude description of octatetraene are given by eqn. (17). The 8 π electrons fill the $n = 1$ to $n = 4$ levels. The lowest electronic transition, $n = 5 \leftarrow n = 4$, corresponds to $E_5^0 - E_4^0 = 21,987 \text{ cm}^{-1}$ which

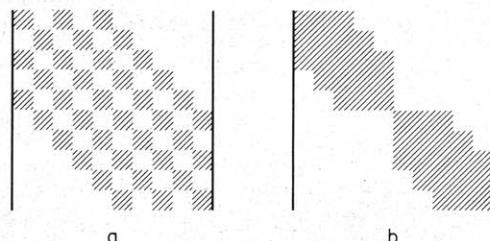


Figure 2. The form of 10×10 secular determinants for the quartic oscillator. To obtain (a) the basis functions were not ordered. In (b) a block diagonal form for the determinant was obtained by ordering the basis functions into even and odd sets.

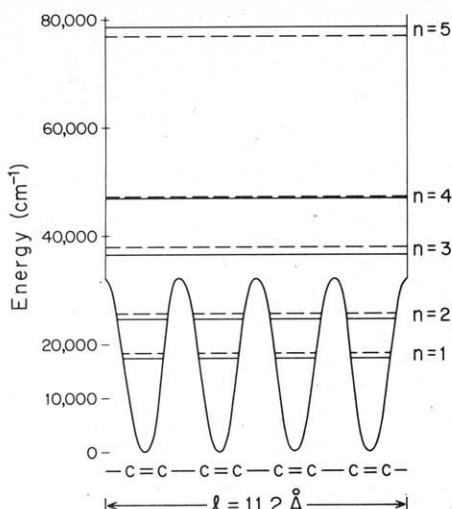


Figure 3. Semi-empirical estimates of the pi-electron energy levels of octatetraene using the free-electron molecular (FEMO) orbital model. The dashed line energy levels are obtained from first order perturbation theory. The solid line energy levels were obtained using the linear variation treatment.

is in poor agreement with the observed $\pi^* \leftarrow \pi$ transition at 33,100 cm⁻¹ (13).

The particle-in-the-box model can be improved by modifying the potential V to be

$$V = \frac{V_o}{2} \left(1 + \cos \frac{8\pi x}{l}\right) \quad 0 \leq x \leq l \\ V = \infty \text{ everywhere else}$$
(18)

which has the effect of causing more electron density in the region of the double bonds than in the single bond regions. A value of $V_o = 32,000$ cm⁻¹ was selected because it fits a whole series of polyene spectral data (13). This potential is shown in Figure 3. First order perturbation theory gives for the energy levels

$$E_n \approx E_n^0 + E_n^1 = \frac{n^2 \pi^2 \hbar^2}{2ml^2} + \int \psi_n^0 V \psi_n^0 d\tau \quad (19)$$

illustrated in Figure 3. The calculated transition ($E_5^0 + E_1^1$) - ($E_4^0 + E_4^1$) = 29,987 cm⁻¹ is a considerable improvement over the unperturbed result. However some of the discrepancy results from the crude determination of energy levels by first order perturbation theory. An accurate determination of the energy levels influenced by the cosinusoidal potential energy of eqn. (18) may be obtained easily by using the linear variation method.

The trial function is an expansion into the particle-in-a-box wavefunctions of eqn. (16), with $f_1 = \psi_1^0, f_2 = \psi_2^0, \dots, f_n = \psi_n^0$. The basis functions are orthonormal so $S_{mn} = \delta_{mn}$ and the energy matrix elements are found to be

$$H_{nn'} = \langle \psi_n^0 | \hat{H}^0 + V | \psi_{n'}^0 \rangle = \left[\left(\frac{\pi^2 \hbar^2}{2ml^2} \right) n^2 + \frac{V_o}{2} \right] \delta_{nn'} + \frac{V_o}{4} \delta_{8,|n-n'|} - \frac{V_o}{4} \delta_{8,n+n'} \quad (20)$$

The energy level from an expansion of the trial function into $n = 10$ basis functions is shown in Figure 3. The transition energy, $W_5 - W_4 = 31,573$ cm⁻¹, changes only slightly in increasing the number of basis functions. The difference between this result and the observed transition at 33,100 cm⁻¹ is therefore due to the FEMO model we have chosen rather than calculation errors.

Figure 3 provides a comparison of perturbation theory and the linear variation method. First order perturbation theory has yielded the approximate energies readily since only eqn. (19) was needed in the evaluation. The linear variation method required the evaluation of a number of matrix elements as well as solving the secular equation. However the variation method gives us accurate results, and MacDonald's theorem assures that we have an upper limit to the true energies of our Hamiltonian. Perturbation theory yields poorer results and the energy levels are either above or below the "exact" values, as

we can see from Figure 3, and we have no theorem to indicate the direction of the approximation errors.

Further experiments with octatetraene may be performed to learn what basis functions are most effective in yielding an accurate energy level by analogy with the quartic oscillator problem. Is it possible to block diagonalize the determinant by appropriate ordering of the basis functions? A study of the shift of energy levels as a function of V_o is informative. Examination of the eigenfunctions to learn what functions are mixed in is revealing. The calculations can of course be applied to the other polyenes from ethylene to vitamin A.

The literature (13) is filled with applications of FEMO to cyclic conjugated systems which also may be treated by linear variation techniques.

Hindered Motions: The Rotational Stark Effect

When an electric field is applied to a sample of molecules whose rotational spectrum is being recorded, shifts and splittings of the lines are observed. The solution to this problem makes use of the linear variation method and is known to those familiar with microwave spectroscopy (14). Simple examples of hindered rotation problems may be found in the literature (15, 16). Other linear variation experiments which explore splitting of angular momentum states include the Stark effect of the hydrogen atom (2, 6). Ligand field or crystal field problems (17) are closely related to these examples.

The Hylleraas Problem

The pioneering work on helium was done by Hylleraas (18) in the late 1920's. Because the Hamiltonian (given here in atomic units) contains the $1/r_{12}$ term which describes the repulsion of the two electrons,

$$\hat{H} = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_{12}} \quad (21)$$

The Schrödinger equation has not been solved analytically. Hylleraas used variational functions that contained the interelectronic distance r_{12} explicitly. They show a dependence on the correlation between the motion of the two electrons and go beyond Hartree-Fock treatments. The six term Hylleraas wave function (20)

$$\phi = e^{-\xi r_1} e^{-\xi r_2} \{ c_1 + c_2(r_1 + r_2) + c_3 r_{12} + c_4(c_1^2 + r_2^2) + c_5 r_1 r_2 + c_6 r_{12}^2 \} \quad \xi = 1.82 \quad (22)$$

can be used also to provide a striking example of the power of the linear variation method. One can do successive 1, 2, ..., 6 term calculations of the energy of the helium ground state atom,³ from which one can see clearly the convergence toward the laboratory experimental result and obtain an energy which is superior to all but the most recent configuration interaction calculations employing expansions of lengths greater than 100 basis functions. In addition, the calculations demonstrate the effect of electron correlation, which is to make the wave function depend explicitly on the distance between the electrons, in such a way as to decrease the value of the wave function when the electrons are close together and to increase its value when the electrons are far from each other.

Hückel Molecular Orbital Calculations

Hückel Molecular Orbital (HMO) calculations are probably the most popular quantum chemistry exercise. The subject is discussed even in introductory chemistry texts and in many monographs (20). Special computer programs have been offered in this Journal (21-22), yet the same linear variation program we have presented will do the job nicely.

As an illustration let us consider the HMO calculations of pyridine.

The Hamiltonian (6) in the HMO method deals only with the π electrons which are n_π in number and is written as the sum

$$\hat{H}_\pi = \sum_{i=1}^{n_\pi} \hat{H}^{\text{eff}}(i) \quad (23)$$

Since the π electrons are treated independently, the Hückel MO's, ϕ_i , satisfy

$$\hat{H}^{\text{eff}}(i) \phi_i = e_i \phi_i \quad (24)$$

where e_i gives the energy of each level. The MO's are written as a sum of $2p_\pi$ atomic orbitals of the n interacting atoms

$$\phi_i = \sum_{r=1}^n c_{ir} f_r \quad (25)$$

where f_r is the atomic orbital on the r^{th} atom.

The matrix elements are written down in the usual way. The Coulomb integral is,

³ Matrix elements and a table of results can be obtained from the authors upon request.

$$H_{rr}^{\text{eff}} = \int f_r(i) \hat{H}_{(i)}^{\text{eff}} f_r(i) d\nu_i = \alpha_C \text{ if } r \text{ is a carbon atom} \\ = \alpha_N = (3/2)\beta_{CC} + \alpha_C \text{ if } r \text{ is a nitrogen atom.} \quad (26)$$

The resonance or bond integral is

$$H_{rs}^{\text{eff}} = \int f_r(i) \hat{H}_{(i)}^{\text{eff}} f_s(i) d\nu_i = \beta_{CC} \text{ for } C_r \text{ and } C_s \text{ bonded} \\ = \beta_{CN} = (4/5)\beta_{CC} \text{ for } C_r \text{ and } N_s \text{ bonded} \\ = 0 \text{ otherwise.} \quad (27)$$

The $2p_z$ orbitals are taken to be orthonormal,

$$S_{rs} = \int f_r(i) f_s(i) d\nu_i = \delta_{rs} \quad (28)$$

The Coulomb integral for the electron associated with carbon is α_C but is increased (6) (somewhat arbitrarily), to $(3/2)\alpha_{CC} + \alpha_C$ to account for the increased electronegativity of the nitrogen atom. The resonance integral for the C—C bond is also different for that of the C—N bond. The small problem that results because our matrix elements are given as symbols, which the computer cannot handle, is solved by writing W in units of β_{CC} and shifting each level by α_C . This is equivalent to the substitution, $W = (E - \alpha_{CC})/\beta_{CC}$, and the secular determinant eqn. (7) becomes

$$\begin{vmatrix} -W & 1 & 0 & 0 & 0 & 1 \\ 1 & -W & 1 & 0 & 0 & 0 \\ 0 & 1 & -W & 4/5 & 0 & 0 \\ 0 & 0 & 4/5 & (3/2-W) & 4/5 & 0 \\ 0 & 0 & 0 & 4/5 & -W & 1 \\ 1 & 0 & 0 & 0 & 1 & -W \end{vmatrix} = 0 \quad (29)$$

The eigenvalues and eigenfunctions of this HMO calculation of pyridine are given in the Table. The eigenvalues are correlated to those of benzene in Figure 4. Pyridine is more strongly bound by its π electrons than benzene essentially because nitrogen is more electronegative than carbon. The double degeneracy of the e_{1u} benzene levels is also lifted.

The assignment of the symmetry species of pyridine follows directly from the form of the eigenfunctions listed in the table. These molecular orbitals are sketched in Figure 5. The diameter of the circle is proportional to the c_{ir} coefficients. The shaded circles indicate that the sign of the $2p_z$ lobe above the plane of the paper is negative while the open circles indicate this lobe is positive. Since pyridine belongs to the C_{2v} group all representations, (a_1 , a_2 , b_1 and b_2) are nondegenerate. Since either reflection of ϕ_1 in the plane of the molecule or rotation by 180° about an axis containing N and C_1 changes its sign, this molecular orbital must belong to b_1 according to the character table (6). The other ϕ_i 's are classified readily.

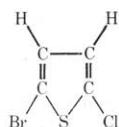
An interesting experiment is to show that if ϕ_1 , ϕ_2 , ϕ_4 , ϕ_6 (belonging to b_1) and ϕ_3 , ϕ_5 (belonging to a_2) are used as basis functions rather than f_1, \dots, f_6 the 6×6 determinant becomes block diagonal. A 4×4 containing only the b_1 MO's and a 2×2 containing the a_2 MO's results. This illustrates one of the basic theorems of group theory which states that $H_{ij} = 0$ and $S_{ij} = 0$ if ϕ_i and ϕ_j belong to different symmetry species (3, 6, 17).

Further examples of MO calculations are obvious. Pi electron densities and bond orders follow directly from the c_{ir} coefficients. Valuable exercises can be constructed using the extended Hückel method (23) since all that is required is more elaborate rules for writing down the H_{ij} and S_{ij} elements.

Analysis of Magnetic Resonance Spectrum

The linear variation method is the standard technique for calculating nmr and esr spectra. Computer programs and algebraic devices are discussed elsewhere for solving the secular equations and generating theoretical spectra (24, 25). However the problems presented by resonance spectra can be solved easily by using the methods we have already outlined.

For our illustration, let us consider the proton magnetic resonance spectrum of 2-bromo-5-chlorothiophene (24),



This molecule has two protons which experience different magnetic fields and are assigned chemical shifts, σ_A and σ_B . The interactions of the nuclear spins of these protons is specified through the coupling constant, J . The spin Hamiltonian is given by

$$\hat{H} = -\nu_o(1 - \sigma_A)I_{zA} - \nu_o(1 - \sigma_B)I_{zB} + J\hat{I}_A \cdot \hat{I}_B \quad (30)$$

where \hat{I}_A and \hat{I}_B are the operators for the total nuclear spin angular

HMO Eigenvalues and Eigenfunctions of Pyridine

$e_1 = \alpha + 2.3\beta$	$\phi_1 = 0.22f_4 + 0.26f_2 + 0.37f_3 + 0.74f_4 + 0.37f_5 + 0.26f_6$
$e_2 = \alpha + 1.44\beta$	$\phi_2 = 0.60f_1 + 0.43f_2 + 0.02f_3 - 0.51f_4 + 0.02f_5 + 0.43f_6$
$e_3 = \alpha + \beta$	$\phi_3 = -0.50f_2 - 0.50f_3 + 0.50f_5 + 0.50f_6$
$e_4 = \alpha - 0.43\beta$	$\phi_4 = 0.55f_1 - 0.12f_2 - 0.50f_3 + 0.41f_4 - 0.50f_5 - 0.12f_6$
$e_5 = \alpha - \beta$	$\phi_5 = +0.50f_2 - 0.50f_3 + 0.50f_5 - 0.50f_6$
$e_6 = \alpha - 1.81\beta$	$\phi_6 = 0.53f_1 - 0.48f_2 + 0.34f_3 - 0.16f_4 + 0.34f_5 - 0.48f_6$

$$e_6 = d - 2\beta \quad e_6 = d - 1.81\beta$$

$$e_4, e_5 = d - \beta \quad e_5 = d - \beta \quad e_4 = d - .43\beta$$

$$e_2, e_3 = d + \beta \quad e_3 = d + \beta \quad e_2 = d + 1.44\beta$$

$$e_1 = d + 2\beta \quad e_1 = d + 2.30\beta$$



Figure 4. Correlation diagram for benzene and pyridine from Hückel MO calculations.

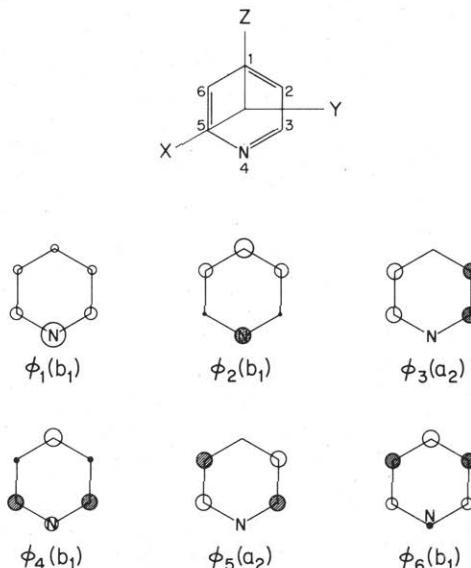


Figure 5. Symmetry of the Hückel molecular orbitals of pyridine.

momentum of protons A and B and I_{zA} and I_{zB} are the operators for the components of spin angular momentum along the axis of the applied magnetic field. Using a fixed frequency $\nu_o = 30.5$ MHz of the resonance spectrometer, the observed spectrum can be explained using $|\sigma_A - \sigma_B| = 1.54 \times 10^{-7}$ and $|J| = 3.9$ Hz as we shall see.

The basis functions used in the expansion of eqn. (2) are formed from the proton spin functions, where $f_1 = |\alpha\alpha\rangle$ indicates α spins for A and B, $f_2 = |\alpha\beta\rangle$ indicates α spin for A and β spin for B and so on: $f_3 = |\beta\alpha\rangle$, $f_4 = |\beta\beta\rangle$. These functions are orthonormal, so for eqn. (5) we have $S_{ij} = \delta_{ij}$. In previous examples the expansion of ϕ was in terms of a long series of basis functions truncated to keep the secular determinant to a reasonable size. Here the four bases functions form a complete set and the accuracy of the energy values that result from solving eqn. (6) and (7) is limited only by computer errors—usually less than 1 part in 10 (12). In all magnetic resonance problems the complete set of basis functions is usually fairly small.

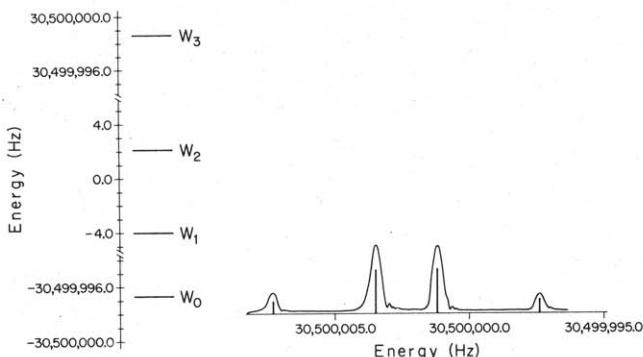


Figure 6. The proton magnetic resonance spectrum of 2-bromo-5-chlorothiophene.

The energy matrix elements of eqn. (4) from the Hamiltonian of eqn. (30) are obtained by the usual spin operator techniques (6, 24, 25).

$$\begin{aligned}
 H_{11} &= \nu_0(-1 + \frac{1}{2}\sigma_A + \frac{1}{2}\sigma_B) + \frac{1}{4}J \\
 H_{22} &= -\frac{1}{2}\nu_0(\sigma_A - \sigma_B) - \frac{1}{4}J \\
 H_{23} &= H_{32} = \frac{1}{2}J \\
 H_{33} &= \frac{1}{2}\nu_0(\sigma_A - \sigma_B) - \frac{1}{4}J \\
 H_{44} &= \nu_0(1 - \frac{1}{2}\sigma_A - \frac{1}{2}\sigma_B) + \frac{1}{4}J
 \end{aligned} \quad (31)$$

Since the chemical shifts are measured relative to some standard we can successfully discuss the splitting pattern by arbitrarily setting one of them, say σ_B , equal to zero. We therefore have $\sigma_A = 1.54 \times 10^{-7}$. The eigenvalues (in Hz) and eigenvectors which result are.

$$\begin{array}{ll}
 W_0 = & -30,499,996.7 \quad \phi_0 = |\alpha\alpha\rangle \\
 W_1 = & -4.0 \quad \phi_1 = 0.94|\alpha\beta\rangle - 0.34|\beta\alpha\rangle \\
 W_2 = & 2.1 \quad \phi_2 = 0.34|\alpha\beta\rangle + 0.94|\beta\alpha\rangle \\
 W_3 = & 4.0 \quad \phi_3 = |\beta\beta\rangle
 \end{array}$$

The eigenvalues given the energy levels as shown in Figure 6. The spectrum may be calculated from the eigenvectors using the usual relationship (24, 25)

$$|\langle \phi_i | I_{XA} + I_{XB} | \phi_j \rangle|^2$$

which is proportional to the intensity of the ($j \rightarrow i$) transition. The calculated stick figure spectrum is superimposed in the observed spectrum in Figure 6. The agreement is excellent.

Other magnetic resonance spectra can be analyzed by analogous methods. While other mathematical methods may generate spectra more rapidly, our simple program does the job directly, and in a manner we feel that it is easy to understand.

Conclusion

The representative experiments that we have described above should serve to illustrate the versatility of the linear variation method and the ease with which it can be applied using a single program package. We feel that these experiments, and others like them, can be an important learning experience in the study of quantum chemistry.

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