

Solve the Secular Equations: $\mathcal{H}\Psi = E\mathcal{S}\Psi$

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Introduction

A general eigenvalue problem is given by $\underline{\underline{A}} \underline{\underline{x}}_i = \lambda_i \underline{\underline{B}} \underline{\underline{x}}_i$, where $\underline{\underline{A}}$ and $\underline{\underline{B}}$ are symmetric matrices, and $\underline{\underline{x}}_i$ is an eigenvector with eigenvalue λ_i . This applet solves this general matrix equation. While not specific to molecular orbital theory, the applet finds its use primarily in solving the secular equation that arises from extended Hückel molecular orbital theory:

$\underline{\underline{H}} \underline{\underline{c}}_j = E_j \underline{\underline{S}} \underline{\underline{c}}_j$. In the secular equation, $\underline{\underline{H}}$ is the matrix of Hamiltonian integrals, $\underline{\underline{S}}$ is the overlap matrix, $\underline{\underline{c}}_j$ are the molecular orbital coefficients, and E_j are the corresponding eigenvalues.

Extended Hückel Molecular Orbital Theory

The extended Hückel method is a useful teaching tool that introduces important concepts used in more rigorous electronic structure methods. Extended Hückel theory is applicable to both σ - and π -molecular orbitals and easily incorporates all the atoms in the periodic table. While not as rigorous as MNDO, AM1, PM3, or *ab initio* methods, extended Hückel calculations are commonly used for an initial approach to polymers, large macrocyclic systems, solids, and surfaces.¹ The first step is to note that the atomic integrals in the secular equations, H_{ii} , are approximately given by valence atomic orbital ionization energies, VOIEs, Table 1.

Table 1*: Valence Orbital Ionization Energies.^{2,3}

Atom	1s	2s	2p
H	13.60		
He	24.5		
Li		5.45	3.50
Be		9.30	6.00
B		14.0	8.30
C		19.5	10.7
N		25.5	13.1
O		32.3	15.9
F		40.4	18.7

* Additional values listed in the Applet

These VOIEs are the configuration averaged energy necessary to remove an electron from a specific atomic orbital in a given atom. For example, the VOIE for the 2p-orbital of carbon is the ionization energy for the gas phase process:

$$C(1s^2 2s^2 2p^2) \rightarrow C^+(1s^2 2s^2 2p^1) + 1 e^-$$

$$\text{VOIE} = E^+(1s^2 2s^2 2p^1)_{\text{averaged}} - E(1s^2 2s^2 2p^2)_{\text{averaged}} \quad (1)$$

The energies of the atom and the cation are averaged over all electronic terms with the same configuration. For the C-atom, the configurations are 3P_0 , 3P_1 , 3P_2 , 1D_2 , 1S_0 . The averages are weighted by the degeneracy of each term, $g_J = 2J + 1$.

The resonance integral is expected to be proportional to the degree of atomic orbital overlap, S_{ij} . A rough approximation for the resonance integral between atoms i and j is:

$$H_{ij} = K S_{ij} \frac{(H_{ii} + H_{jj})}{2} \quad (2)$$

where K is often approximated as 1.75. Using VOIEs to approximate the atomic and resonance integrals then allows the extended method to be applied to all elements.

The molecular orbitals are given by the LCAO approximation: $\Psi_{\text{MO},i} = \sum c_{ij} \phi_j$. For example for two atomic orbitals A and B, molecular orbital i is $\Psi_{\text{MO},i} = c_{iA} \phi_A + c_{iB} \phi_B$. The matrix form of the LCAO secular equations with two orbitals is:

$$\begin{pmatrix} H_{AA} - E_i S_{AA} & H_{AB} - E_i S_{AB} \\ H_{AB} - E_i S_{AB} & H_{BB} - E_i S_{BB} \end{pmatrix} \begin{pmatrix} c_{iA} \\ c_{iB} \end{pmatrix} = 0 \quad (3)$$

This equation can be factored and rearranged to give:

$$\begin{pmatrix} H_{AA} & H_{AB} \\ H_{AB} & H_{BB} \end{pmatrix} \begin{pmatrix} c_{iA} \\ c_{iB} \end{pmatrix} - E_i \begin{pmatrix} S_{AA} & S_{AB} \\ S_{AB} & S_{BB} \end{pmatrix} \begin{pmatrix} c_{iA} \\ c_{iB} \end{pmatrix} = 0$$

and

$$\begin{pmatrix} H_{AA} & H_{AB} \\ H_{AB} & H_{BB} \end{pmatrix} \begin{pmatrix} c_{iA} \\ c_{iB} \end{pmatrix} = E_i \begin{pmatrix} S_{AA} & S_{AB} \\ S_{AB} & S_{BB} \end{pmatrix} \begin{pmatrix} c_{iA} \\ c_{iB} \end{pmatrix} \quad (4)$$

If we let $\underline{\underline{H}}$ be the matrix of the Hamiltonian integrals, $\underline{\underline{S}}$ the overlap matrix, and $\underline{\underline{c}}_i$ be the vector of molecular orbital coefficients for eigenstate i , this matrix equation becomes:

$$\underline{\underline{H}} \underline{\underline{c}}_i = E_i \underline{\underline{S}} \underline{\underline{c}}_i \quad (5)$$

Multiplying from the left by the inverse of the overlap matrix and using $\underline{\underline{S}}^{-1} \underline{\underline{S}} = 1$, gives:

$$(\underline{\underline{S}}^{-1} \underline{\underline{H}}) \underline{\underline{c}}_i = E_i \underline{\underline{c}}_i \quad (6)$$

The molecular orbitals and energies are then the eigenvectors and eigenvalues of the matrix $(\underline{\underline{S}}^{-1} \underline{\underline{H}})$. Eq. 6 is easily solved using general matrix methods. Unfortunately, the extended Hückel method does not include the effects of electron spin, so electron exchange and correlation interactions are not included in the method.

Instruction for Using the Applet

The following two examples provide a quick starting point. In the first example, we fill in the $\underline{\underline{S}}$ and $\underline{\underline{H}}$ matrices by hand. In the second example, we use the "Generate H" button to fill in the $\underline{\underline{H}}$ matrix. Atomic symbols and orbital type labels are not required if you fill in the Hamiltonian matrix by hand. The atom labels are then only used, if you choose, to label the coefficients of the listed eigenvectors. When using the "Generate H" button, the atomic symbols and orbital types act as pointers to look up the VOIE for the specified atomic orbital.

Manual entry of both matrices is the most flexible. You can use any method you choose for calculating the matrix elements. The “Generate H” button simply is a time-saving convenience that uses the tabulated VOIE values and Eq. 2 to calculate the matrix elements.

Example 1: Lithium Hydride, LiH

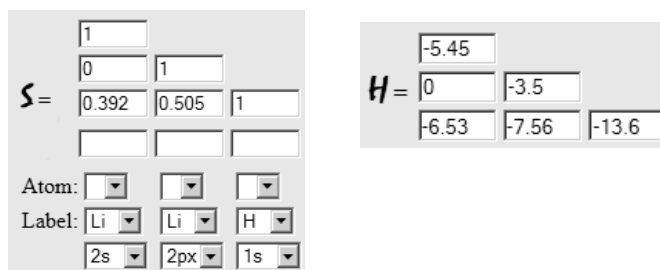
Calculate the bond order in lithium hydride, LiH. For a bond length of 1.61 Å, the H(1s)- Li(2s) overlap integral is 0.392 and the H(1s)- Li(2p_x) overlap is 0.505.

Answer: The valence orbital ionization energies are listed in Table 1. At this low level of approximation, the energies of the Li(2p_y) and Li(2p_z) are unaffected by the electrons in the σ-molecular orbitals. Because the 2p_y and 2p_z are non-interacting, we don't need to include them in the secular equations. The resonance integrals are given using Eq. 2 and K = 1.75 as:

$$\text{H(1s)- Li(2s):} \quad H_{1s,2s} = K S_{ij} \frac{(H_{ii} + H_{jj})}{2} = 1.75(0.392) \frac{(-5.45 + (-13.6))}{2} \text{ eV} = -6.53 \text{ eV}$$

$$\text{H(1s)- Li(2p}_x\text{):} \quad H_{1s,2p_x} = 1.75(0.505) \frac{(-3.50 + (-13.6))}{2} \text{ eV} = -7.56 \text{ eV}$$

The “Secular” applet input set-up is:



The labels are optional; in this case they are simply used to label the orbitals in the output for easier reading. The output of the applet is:

```

Eigenvalues and eigenvectors
_____(eigenvectors listed in columns)_____
E(i)   -13.7867   -4.7341   5.2162
vector  1         2         3
atom:
Li2s    0.1336    0.8348    0.4630
Li2px   0.0575    -0.5355    0.6737
H1s     0.9894    -0.1279   -0.5760

```

The bond order between atom-a and -b is approximated by the **Mulliken overlap population**, P_{ab} . The overlap population is given by the sum over all atomic orbitals j on atom-a and atomic orbitals k on atom-b and the sum over all molecular orbitals i with occupancy n_i :

$$P_{ab} = \sum_{j \text{ on a}} \sum_{k \text{ on b}} \sum_{i=1}^m n_i 2 c_{ij} c_{ik} S_{jk} \quad \text{for atoms a and b and MO i with } n_i \text{ electrons}$$

$$j = \text{all atomic orbitals on atom-a} \quad (7)$$

$$k = \text{all atomic orbitals on atom-b}$$

With two valence electrons, only the lowest energy orbital is filled. The bond order is given by:

$$P_{\text{LiH}} = 4 c_{1,2s\text{Li}} c_{1,1s\text{H}} S_{2s\text{Li},1s\text{H}} + 4 c_{1,2p_x\text{Li}} c_{1,1s\text{H}} S_{2p_x\text{Li},1s\text{H}} \quad (8)$$

$$= 4(0.1336)(0.9894)(0.392) + 4(0.0575)(0.9894)(0.505) = 0.322$$

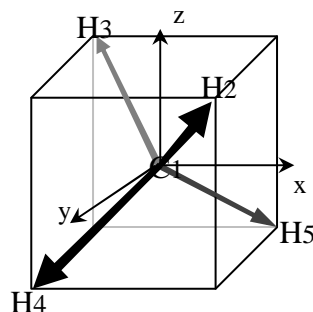
The extended Hückel bond order of 0.322 is significantly smaller than the CNDO bond order of 0.611. The CNDO bond order is more realistic, but the extended Hückel result is easy to calculate and applicable to elements that are not available in common semi-empirical methods. In general, bond orders are often underestimated by the extended Hückel approach.

Example 2: Methane, CH₄

Calculate the charge on the C-atom in methane.

Answer: The atomic coordinates for methane with a C-H bond length of 1.084 Å are:

C	0.000000	0.000000	0.000000
H	0.625651	0.625651	0.625651
H	-0.625651	-0.625651	0.625651
H	-0.625651	0.625651	-0.625651
H	0.625651	-0.625651	-0.625651



The hydrogen atoms are placed at the opposing corners of a cube that has faces oriented perpendicular to the axes. To quickly determine the overlap integrals, we can use the atomic coordinates as input for the “*cndo*” applet. The “*cndo*” applet lists overlap integrals. Yes, we know that using a more advanced level of approximation to get the overlap integrals for a lower-level extended Hückel calculation is cheating, but the instructional value of the extended Hückel calculation is undiminished. The overlap matrix is:

	1 C2s	1 C2p _x	1 C2p _y	1 C2p _z	2 H1s	3 H1s	4 H1s	5 H1s
1 C2s	1.0	0.0	0.0	0.0	0.5224	0.5224	0.5224	0.5224
1 C2p _x	0.0	1.0	0.0	0.0	0.2832	-0.2832	-0.2832	0.2832
1 C2p _y	0.0	0.0	1.0	0.0	0.2832	-0.2832	0.2832	-0.2832
1 C2p _z	0.0	0.0	0.0	1.0	0.2832	0.2832	-0.2832	-0.2832
2 H1s	0.5224	0.2832	0.2832	0.2832	1.0	0.1877	0.1877	0.1877
3 H1s	0.5224	-0.2832	-0.2832	0.2832	0.1877	1.0	0.1877	0.1877
4 H1s	0.5224	-0.2832	0.2832	-0.2832	0.1877	0.1877	1.0	0.1877
5 H1s	0.5224	0.2832	-0.2832	-0.2832	0.1877	0.1877	0.1877	1.0

Notice that the C(2s)-H(1s) overlaps are all identical, as expected, while the C(2p)-H(1s) differ only in sign. Adjacent pairs of H-atoms have a significant overlap, 0.1877, as expected from VSEPR theory. Entering these overlap integrals into the “*Secular*” applet gives:

S =

Atom:
Label:

Using the Generate H option, the Hamiltonian matrix is:

H =

The final output is:

Eigenvalues and eigenvectors
(eigenvectors listed in columns)

E(i)	-23.2715	-14.9487	-14.9487	-14.9487	6.44	6.44	6.44	35.4649
vector	1	2	3	4	5	6	7	8
atom:								
C2s	0.8444	0.0	0.0	-0.0	0.0	-0.0	0.0	0.7746
C2px	-0.0	-0.0623	0.6373	0.0684	-0.5167	0.0307	0.4336	0.0
C2py	-0.0	-0.6387	-0.0561	-0.0595	0.2014	-0.58	0.2811	-0.0
C2pz	-0.0	0.053	0.0736	-0.6375	0.3852	0.3444	0.4347	0.0
H1s	0.2678	-0.385	0.389	-0.3734	-0.0381	0.1119	-0.6277	-0.3162
H1s	0.2678	0.4479	-0.3015	-0.384	-0.3826	-0.4881	0.1529	-0.3162
H1s	0.2678	-0.3739	-0.4556	0.3027	-0.1819	0.5216	0.3207	-0.3162
H1s	0.2678	0.3109	0.3681	0.4547	0.6026	-0.1454	0.1541	-0.3162

Notice that the MOs involve C(2s) character or C(2p) character, but not both, in contradiction to hybridization arguments.

The atom electron density for atom-a is calculated as the sum over all atomic orbitals j on atom-a and the sum over all molecular orbitals i:

$$d_a = \sum_{j \text{ on a}} \sum_{i=1}^m n_i c_{ij}^2 \quad j = \text{all atomic orbitals on atom-a} \quad (9)$$

With 8 valence electrons, the HOMO is orbital 4. The atom electron density on the C-atom is:

$$\begin{aligned}
 d_C &= 2(0.8444)^2 && \text{contribution from C(2s)} \\
 &+ 2(-0.0623)^2 + 2(0.6373)^2 + 2(0.0684)^2 && \text{contribution from C(2p}_x\text{)} \\
 &+ 2(-0.6387)^2 + 2(-0.0561)^2 + 2(-0.0595)^2 && \text{contribution from C(2p}_y\text{)} \\
 &+ 2(0.0530)^2 + 2(0.0736)^2 + 2(-0.6375)^2 && \text{contribution from C(2p}_z\text{)}
 \end{aligned}$$

$$d_C = 3.9137$$

The contributions from the $C(2p_x)$, $C(2p_y)$, and $C(2p_z)$ are identical, as expected by symmetry. Since carbon has four valence electrons, the charge on the C-atom is $4 - 3.9137 = +0.0862$. For comparison, the charge at the CNDO level is -0.052 .

The bond length chosen for this example is the HF/6-31G(d) minimized structure.

Frequently Asked Questions

1. Is there a difference between $2p_x$, $2p_y$, and $2p_z$ -type orbitals?

No, for the purposes of constructing the Hamiltonian matrix, the atom labels just determine which VOIEs to select for the diagonal matrix elements. The VOIEs for a $2p_x$, $2p_y$, and $2p_z$ orbital are identical. The x, y, z-distinction is included to help label the output eigenvectors for easier readability.

2. Why are the atomic coordinates not needed for the applet input?

One of the important educational objectives of this applet is to underscore the flow of information in molecular orbital calculations. The atomic coordinates are necessary to calculate the overlap integrals. However, calculating the overlap integrals is the only point that bond lengths and angles enter into the calculation, if the atomic integrals are approximated by VOIEs and the resonance integrals are calculated using Eq. 2.

3. What are the energy units?

The units of the energy are the same as the Hamiltonian matrix elements. Using the VOIEs in the Table in eV produces eigenvalues in units of eV. Overlap integrals and eigenvector coefficients are unitless, since $\int \Psi^* \Psi \, d\tau$ represents a probability.

4. Why allow only eight orbitals?

Several excellent extended Hückel programs are readily available, including ICON-EDit by Gion Calzaferri's group and YAeHMOP by Roald Hoffmann's group.^{4,5} These programs are general purpose approaches that include several important and useful extensions of the method. Most notably, these more complete programs allow the atomic integrals to vary with the charge on the atom, instead of using fixed VOIEs. These programs input the atom coordinates and include the calculation of the overlap integrals. The "*Secular*" applet is meant as an instructional tool that avoids the "black-box" appearance of the larger programs. The applet may be easily edited to include larger matrices if needed.

5. Why only symmetric matrices?

The general eigenvalue problem is more difficult to solve for non-symmetric matrices. The secular equations from the LCAO-MO approach are always symmetrical.

6. Why are the complex components of the eigenvectors not listed?

The general eigenvalue problem can result in complex eigenvectors. The solution of the LCAO-secular equations in the extended Hückel approximation produces only real components. The complex portions of the eigenvectors are calculated and may be listed if desired by editing the source code. The \underline{S} matrix must be positive definite (because Cholesky decomposition is used to solve the simultaneous set of equations).

Literature Cited:

1. R. Hoffman, *Solids and Surfaces, A Chemists View of Bonding in Extended Structures*, VCH, New York, NY, 1988.
2. H. B. Gray, *Electrons and Chemical Bonding*, Benjamin/Cummings, Menlo Park, CA, 1964, Appendix.
3. R. L. DeKock, H. B. Gray, *Chemical Structure and Bonding*, Benjamin/Cummings, Menlo Park, CA, 1980, p. 227.
4. [/www.groups.dcb.unibe.ch/groups/calzaferri//program/iconedit.html](http://www.groups.dcb.unibe.ch/groups/calzaferri//program/iconedit.html), last accessed 8/19/2013.
5. <http://www.roaldhoffmann.com/> and <http://yaehmop.sourceforge.net/> last accessed 8/19/2013.