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Butadiene via the Huckel Scheme (using Maple)

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I. SYNOPSIS

The Hückel Molecular Orbital Scheme is discussed analytically and using Maple in the context of butadiene, as a precursor (partially) to discussing the Woodward-Hoffman electrocyclic ring closure rules.

II. INTRODUCTION

We define the coordinate system so that carbons 1 and 4 define the z-axis, and the x-y plane bisects the 1-4 line. This means that we are dealing with p_y orbitals when we do normal Hückel computations. Note, this is contrary to normal usage, where the z-axis is usually chosen perpendicular to the carbon plane.

The basis set, shown in Figure 1, represents 4 p orbitals, all parallel to each other, centered on each of the relevant carbon atoms. (Once more, for emphasis, normally, these are considered p_z orbitals, but we will call them p_y because in our future work, the z-axis will be reserved for other use.)

The Hamiltonian for butadiene (in the Hückel approximation) is

$$H_{op} = \begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix} \tag{2.1}$$

so, that, since

$$H_{op}\psi = E\psi$$

leads to

$$\begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix}$$

which, transferring the r.h.s. over to the left hand side gives

$$\begin{pmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = 0$$

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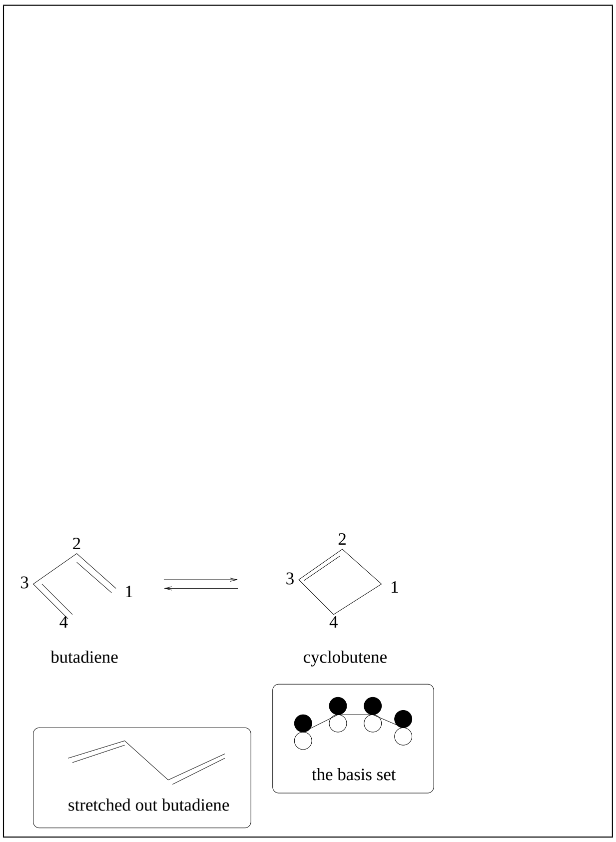

FIG. 1: Naked σ framework and p-electron basis set

where $x = (\alpha - E)/\beta$, results in a secular equation

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$

in the standard form, which here yields a quartic when expanded (by minors), i.e.,

$$(x^2)^2 - 3x^2 + 1 = 0$$

which is quadratic in x^2 with roots

$$x^2 = \frac{3 \pm \sqrt{9-4}}{2}$$

which is

$$x = \pm\sqrt{\frac{3 \pm \sqrt{5}}{2}}$$

This results in four roots:

$$x_{++} = +\sqrt{\frac{3+\sqrt{5}}{2}}$$
$$x_{+-} = +\sqrt{\frac{3-\sqrt{5}}{2}}$$
$$x_{-+} = -\sqrt{\frac{3+\sqrt{5}}{2}}$$
$$x_{--} = -\sqrt{\frac{3-\sqrt{5}}{2}}$$

Before we continue, it is important to realize that Maple does not give this answer. In fact, depending on the textbook, you will find other eigenvalues than those listed here. The "++" eigenvalue, above[1], is cited as $+\frac{1+\sqrt{5}}{2}$ which happens to be the Maple value, *vide infra*, although the value we report ($\sqrt{\frac{3+\sqrt{5}}{2}}$ above) is reported by La Paglia[2] (notice the strange radical inside a radical). Yet one more note. An explanatory discussion of how this computation is done can be found[3] where the actual computation of eigenfunctions is discussed.

At first blush, these are not equal. But they are. Thus

$$\frac{1+\sqrt{5}}{2} = \sqrt{\left(\frac{1+\sqrt{5}}{2}\right)^2}$$

which is

$$\sqrt{\left(\frac{1+2\sqrt{5}+5}{4}\right)} = \sqrt{\left(\frac{6+2\sqrt{5}}{4}\right)} = \sqrt{\left(\frac{3+\sqrt{5}}{2}\right)}$$

so that

$$\frac{1+\sqrt{5}}{2} = \sqrt{\left(\frac{3+\sqrt{5}}{2}\right)} \tag{2.2}$$

We will use the "simpler" form (Gatz) rather than the more complex one we have actually derived.

$$x_{++} = +\frac{1+\sqrt{5}}{2} = 1.618 \equiv +p$$
$$x_{--} = -\frac{1-\sqrt{5}}{2} = 0.618 \equiv -m$$
$$x_{+-} = +\frac{1-\sqrt{5}}{2} = -0.618 \equiv +m$$
$$x_{-+} = -\frac{1+\sqrt{5}}{2} = -1.618 \equiv -p$$

where we have rearranged the order of eigenvalues, and included their numerical values (which are usually cited).

Here is the Maple input which creates these results:

```
restart;
with (linalg):
H := array([[alpha,beta,0,0],
[beta,alpha,beta,0],
[0,beta,alpha,beta],
[0,0,beta,alpha]]);
C := eigenvals(H);
Vecs := eigenvects(H);#works only for rationals etc.
```

and here are the output lines:

$$H := \begin{bmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{bmatrix}$$

$$C := \alpha - \frac{1}{2}\beta + \frac{1}{2}\sqrt{5}\beta,\ \alpha - \frac{1}{2}\beta - \frac{1}{2}\sqrt{5}\beta,\ \alpha + \frac{1}{2}\beta + \frac{1}{2}\sqrt{5}\beta,\ \alpha + \frac{1}{2}\beta - \frac{1}{2}\sqrt{5}\beta$$

$$Vecs := \left[\alpha - \frac{1}{2}\beta + \frac{1}{2}\sqrt{5}\beta,\ 1,\ \left\{\left[-1,\ \frac{\frac{1}{2}\beta - \frac{1}{2}\sqrt{5}\beta}{\beta},\ -\frac{\frac{1}{2}\beta - \frac{1}{2}\sqrt{5}\beta}{\beta},\ 1\right]\right\}\right],$$
$$\left[\alpha - \frac{1}{2}\beta - \frac{1}{2}\sqrt{5}\beta,\ 1,\ \left\{\left[-1,\ \frac{\frac{1}{2}\beta + \frac{1}{2}\sqrt{5}\beta}{\beta},\ -\frac{\frac{1}{2}\beta + \frac{1}{2}\sqrt{5}\beta}{\beta},\ 1\right]\right\}\right],$$
$$\left[\alpha + \frac{1}{2}\beta + \frac{1}{2}\sqrt{5}\beta,\ 1,\ \left\{\left[1,\ -\frac{-\frac{1}{2}\beta - \frac{1}{2}\sqrt{5}\beta}{\beta},\ -\frac{-\frac{1}{2}\beta - \frac{1}{2}\sqrt{5}\beta}{\beta},\ 1\right]\right\}\right],$$

$$\left[\alpha+\frac{1}{2}\beta-\frac{1}{2}\sqrt{5}\beta,\ 1,\ \left\{\left[1,\ -\frac{-\frac{1}{2}\beta+\frac{1}{2}\sqrt{5}\beta}{\beta},\ -\frac{-\frac{1}{2}\beta+\frac{1}{2}\sqrt{5}\beta}{\beta},\ 1\right]\right\}\right]$$

We re-write them in more human form (and leave out the degeneracies):

$$Vecs :=$$

$$\left[\alpha-\frac{1-\sqrt{5}}{2}\beta, \{[-1,\ +m,\ -m,\ 1]\}\right]$$

$$\left[\alpha-\frac{1+\sqrt{5}}{2}\beta, \{[-1,\ +p,\ -p,\ 1]\}\right],$$

$$\left[\alpha+\frac{1+\sqrt{5}}{2}, \{[1,\ +p,\ +p,\ 1]\}\right],$$

$$\left[\alpha+\frac{1-\sqrt{5}}{2}\beta \{[1,\ +m,\ +m,\ 1]\}\right]$$

We rewrite them (one more time) in *even* more human form:

$$Vecs :=$$

$$[\alpha-m\beta, \{[-1, -0.618, +0.618,\ 1]\}]$$

$$[\alpha-p\beta, \{[-1,\ 1.618, -1.618,\ 1]\}],$$

$$[\alpha+p\beta, \{[1,\ 1.618, 1.618,\ 1]\}],$$

$$[\alpha+m\beta \{[1,\ +-0.618, -0.618,\ 1]\}]$$

These can be seen in Figure 2 where the relative signs are shown with filled in spheres + and open spheres -, while the magnitudes are shown by expansion and contraction of the lobes themselves.

The eigenfunction corresponding to the "++" eigenvalue is:

$$\begin{pmatrix}\alpha&\beta&0&0\\\beta&\alpha&\beta&0\\0&\beta&\alpha&\beta\\0&0&\beta&\alpha\end{pmatrix}\otimes\begin{pmatrix}1\\\frac{1+\sqrt{5}}{2}\\\frac{1+\sqrt{5}}{2}\\1\end{pmatrix}=\begin{pmatrix}\alpha+\frac{1+\sqrt{5}}{2}\beta\\\beta+\left(\frac{1+\sqrt{5}}{2}\right)(\alpha+\beta)\\\beta+\left(\frac{1+\sqrt{5}}{2}\right)(\alpha+\beta)\\\alpha+\frac{1+\sqrt{5}}{2}\beta\end{pmatrix} \tag{2.3}$$

which can be checked by direct expansion. Thus, for the second row multiplication we obtain

$$\beta+\left(\frac{1+\sqrt{5}}{2}\right)(\alpha+\beta)=\beta+\frac{1+\sqrt{5}}{2}\beta+\frac{1+\sqrt{5}}{2}\alpha=\left(1+\frac{1+\sqrt{5}}{2}\right)\beta+\frac{1+\sqrt{5}}{2}\alpha$$

We have, using Equation 2.2

$$\left(1+\frac{1+\sqrt{5}}{2}\right)\beta+\frac{1+\sqrt{5}}{2}\alpha=\left(\sqrt{\left(\frac{3+\sqrt{5}}{2}\right)}\right)^2\beta+\frac{1+\sqrt{5}}{2}\alpha$$

$$=\frac{1+\sqrt{5}}{2}\left(\alpha+\frac{1+\sqrt{5}}{2}\beta\right)$$

We then have

$$\begin{pmatrix}\alpha&\beta&0&0\\\beta&\alpha&\beta&0\\0&\beta&\alpha&\beta\\0&0&\beta&\alpha\end{pmatrix}\otimes\begin{pmatrix}1\\\left(\frac{1+\sqrt{5}}{2}\right)\\\left(\frac{1+\sqrt{5}}{2}\right)\\1\end{pmatrix}=\left(\alpha+\frac{1+\sqrt{5}}{2}\beta\right)\begin{pmatrix}1\\\left(\frac{1+\sqrt{5}}{2}\right)\\\left(\frac{1+\sqrt{5}}{2}\right)\\1\end{pmatrix} \tag{2.4}$$

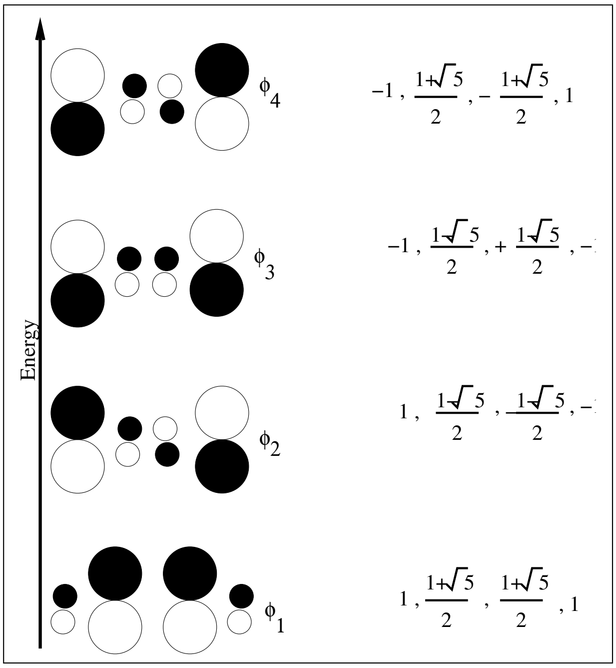

FIG. 2: Eigenfunctions of Butadiene

For the next (+ -) eigenvalue we have

$$\begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix} \otimes \begin{pmatrix} 1 \\ \left(\frac{1-\sqrt{5}}{2}\right) \\ \left(\frac{1-\sqrt{5}}{2}\right) \\ 1 \end{pmatrix} = \left(\alpha + \frac{1-\sqrt{5}}{2}\beta\right) \begin{pmatrix} 1 \\ \left(\frac{1-\sqrt{5}}{2}\right) \\ \left(\frac{1-\sqrt{5}}{2}\right) \\ 1 \end{pmatrix} \tag{2.5}$$

For the next (- +) eigenvalue we have

$$\begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix} \otimes \begin{pmatrix} -1 \\ \left(\frac{1-\sqrt{5}}{2}\right) \\ -\left(\frac{1-\sqrt{5}}{2}\right) \\ 1 \end{pmatrix} = \left(\alpha - \frac{1-\sqrt{5}}{2}\beta\right) \begin{pmatrix} -1 \\ \left(\frac{1-\sqrt{5}}{2}\right) \\ -\left(\frac{1-\sqrt{5}}{2}\right) \\ 1 \end{pmatrix} \tag{2.6}$$

For the last (- -) eigenvalue we have

$$\begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix} \otimes \begin{pmatrix} -1 \\ \left(\frac{1+\sqrt{5}}{2}\right) \\ -\left(\frac{1+\sqrt{5}}{2}\right) \\ 1 \end{pmatrix} = \left(\alpha - \frac{1+\sqrt{5}}{2}\beta\right) \begin{pmatrix} -1 \\ \left(\frac{1+\sqrt{5}}{2}\right) \\ -\left(\frac{1+\sqrt{5}}{2}\right) \\ 1 \end{pmatrix} \tag{2.7}$$

III. AN INTERESTING CONSTRUCT

Let's juxtapose the four eigenvectors thusly:

$$\begin{pmatrix} 1 \\ \left(\frac{1+\sqrt{5}}{2}\right) \\ \left(\frac{1+\sqrt{5}}{2}\right) \\ 1 \end{pmatrix} \begin{pmatrix} 1 \\ \left(\frac{1-\sqrt{5}}{2}\right) \\ \left(\frac{1-\sqrt{5}}{2}\right) \\ 1 \end{pmatrix} \begin{pmatrix} -1 \\ \left(\frac{1-\sqrt{5}}{2}\right) \\ -\left(\frac{1-\sqrt{5}}{2}\right) \\ 1 \end{pmatrix} \begin{pmatrix} -1 \\ \left(\frac{1+\sqrt{5}}{2}\right) \\ -\left(\frac{1+\sqrt{5}}{2}\right) \\ 1 \end{pmatrix}$$

to form a matrix, we'll call it T, i.e.,

$$T = \begin{pmatrix} 1 & 1 & -1 & -1 \\ \left(\frac{1+\sqrt{5}}{2}\right) & \left(\frac{1-\sqrt{5}}{2}\right) & \left(\frac{1-\sqrt{5}}{2}\right) & \left(\frac{1+\sqrt{5}}{2}\right) \\ \left(\frac{1+\sqrt{5}}{2}\right) & \left(\frac{1-\sqrt{5}}{2}\right) & -\left(\frac{1-\sqrt{5}}{2}\right) & -\left(\frac{1+\sqrt{5}}{2}\right) \\ 1 & 1 & 1 & 1 \end{pmatrix}$$

and its transpose:

$$T^{trans} = \begin{pmatrix} 1 & \left(\frac{1+\sqrt{5}}{2}\right) & \left(\frac{1+\sqrt{5}}{2}\right) & 1 \\ 1 & \left(\frac{1-\sqrt{5}}{2}\right) & \left(\frac{1-\sqrt{5}}{2}\right) & 1 \\ -1 & \left(\frac{1-\sqrt{5}}{2}\right) & -\left(\frac{1-\sqrt{5}}{2}\right) & 1 \\ -1 & \left(\frac{1+\sqrt{5}}{2}\right) & -\left(\frac{1+\sqrt{5}}{2}\right) & 1 \end{pmatrix}$$

so that we form the peculiar construct $T^{trans}HT$:

$$\begin{pmatrix} 1 & 1 & -1 & -1 \\ \left(\frac{1+\sqrt{5}}{2}\right) & \left(\frac{1-\sqrt{5}}{2}\right) & \left(\frac{1-\sqrt{5}}{2}\right) & \left(\frac{1+\sqrt{5}}{2}\right) \\ \left(\frac{1+\sqrt{5}}{2}\right) & \left(\frac{1-\sqrt{5}}{2}\right) & -\left(\frac{1-\sqrt{5}}{2}\right) & -\left(\frac{1+\sqrt{5}}{2}\right) \\ 1 & 1 & 1 & 1 \end{pmatrix} \otimes \begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix} \otimes \begin{pmatrix} 1 & \left(\frac{1+\sqrt{5}}{2}\right) & \left(\frac{1+\sqrt{5}}{2}\right) & 1 \\ 1 & \left(\frac{1-\sqrt{5}}{2}\right) & \left(\frac{1-\sqrt{5}}{2}\right) & 1 \\ -1 & \left(\frac{1-\sqrt{5}}{2}\right) & -\left(\frac{1-\sqrt{5}}{2}\right) & 1 \\ -1 & \left(\frac{1+\sqrt{5}}{2}\right) & -\left(\frac{1+\sqrt{5}}{2}\right) & 1 \end{pmatrix}$$

When we carry out this complicated multiplication, a pleasant surprise is in the offing.

IV. MAPLE

A worked example with maple manipulation (kudos to F. W. Chapman, fc03@Lehigh.edu, for materials which helped in this project).

```
> restart;
> #printlvl := 10;#debugging statement, can be omitted
> printlevel := 0;
> with (LinearAlgebra);
```

$$printlevel := 0$$

We allow this printing here so that the reader can see what else is available in the Maple package. This is at the level of Maple 8.

[*Add*, *Adjoint*, *BackwardSubstitute*, *BandMatrix*, *Basis*, *BezoutMatrix*, *BidiagonalForm*, *BilinearForm*, *CharacteristicMatrix*, *CharacteristicPolynomial*, *Column*, *ColumnDimension*, *ColumnOperation*, *ColumnSpace*, *CompanionMatrix*, *ConditionNumber*, *ConstantMatrix*, *ConstantVector*, *CreatePermutation*, *CrossProduct*, *DeleteColumn*, *DeleteRow*, *Determinant*, *DiagonalMatrix*, *Dimension*, *Dimensions*, *DotProduct*, *EigenConditionNumbers*, *Eigenvalues*, *Eigenvectors*, *Equal*, *ForwardSubstitute*, *FrobeniusForm*, *GaussianElimination*, *GenerateEquations*, *GenerateMatrix*, *GetResultDataType*, *GetResultShape*, *GivensRotationMatrix*, *GramSchmidt*, *HankelMatrix*, *HermiteForm*, *HermitianTranspose*, *HessenbergForm*, *HilbertMatrix*, *HouseholderMatrix*, *IdentityMatrix*, *IntersectionBasis*, *IsDefinite*, *IsOrthogonal*, *IsSimilar*, *IsUnitary*, *JordanBlockMatrix*, *JordanForm*, *LA_Main*, *LUDecomposition*, *LeastSquares*, *LinearSolve*, *Map*, *Map2*, *MatrixAdd*, *MatrixInverse*, *MatrixMatrixMultiply*, *MatrixNorm*, *MatrixScalarMultiply*, *MatrixVectorMultiply*, *MinimalPolynomial*, *Minor*, *Modular*, *Multiply*, *NoUserValue*, *Norm*, *Normalize*, *NullSpace*, *OuterProductMatrix*, *Permanent*, *Pivot*, *PopovForm*, *QRDecomposition*, *RandomMatrix*, *RandomVector*, *Rank*, *ReducedRowEchelonForm*, *Row*, *RowDimension*, *RowOperation*, *RowSpace*, *ScalarMatrix*, *ScalarMultiply*, *ScalarVector*, *SchurForm*, *SingularValues*, *SmithForm*, *SubMatrix*, *SubVector*, *SumBasis*, *SylvesterMatrix*, *ToeplitzMatrix*, *Trace*, *Transpose*, *TridiagonalForm*, *UnitVector*, *VandermondeMatrix*, *VectorAdd*, *VectorAngle*, *VectorMatrixMultiply*, *VectorNorm*, *VectorScalarMultiply*, *ZeroMatrix*, *ZeroVector*, *Zip*]

We define the Hamiltonian matrix for butadiene here:

```
> H := Matrix([[alpha,beta,0,0],
> [beta,alpha,beta,0],
> [0,beta,alpha,beta],
> [0,0,beta,alpha]]);
```

$$H := \begin{bmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{bmatrix}$$

Next, we obtain the eigenvalues of the Hamiltonian, and create the diagonalized representative of the Hamiltonian, i.e. the result we expect to obtain if we invoke a properly constructed similarity transformation (at the end).

```
> C := Eigenvalues(H);
  > Vecs := Eigenvectors(H,output='vectors');

#COMMENT We need to normalize these eigenvectors, hence the following code

for i from 1 to LinearAlgebra[ColumnDimension](Vecs) do
  Vecs[1..-1,i]:=LinearAlgebra[Normalize](Vecs[1..-1,i],Euclidean);
  end do;

#COMMENT next, we obtain the transpose of the eigenvector matrix

Vecs_trans := Transpose(Vecs);

#COMMENT and here we do the triple matrix multiplication corresponding
to the similarity transformation (using the T matrix in the body
of the text, above.)

Result := simplify(Multiply(Vecs_trans,Multiply(H,Vecs)));

#COMMENT Lastly, attempt to write the results in a more human readable form.
Notice that the final results mirror results we had in the body of the text.

for i from 1 to 4 do
  Result[i,i] := collect(Result[i,i],[alpha,beta], recursive);
  end do;
  Result;
```

$$C := \begin{bmatrix} \frac{1}{2}\beta + \alpha + \frac{1}{2}\sqrt{5}\,\beta \\ \frac{1}{2}\beta + \alpha - \frac{1}{2}\sqrt{5}\,\beta \\ \alpha - \frac{1}{2}\beta + \frac{1}{2}\sqrt{5}\,\beta \\ \alpha - \frac{1}{2}\beta - \frac{1}{2}\sqrt{5}\,\beta \end{bmatrix}$$

$$Vecs := \begin{bmatrix} 1 & 1 & -1 & -1 \\ -\frac{-\frac{1}{2}\beta - \frac{1}{2}\sqrt{5}\,\beta}{\beta} & -\frac{-\frac{1}{2}\beta + \frac{1}{2}\sqrt{5}\,\beta}{\beta} & \frac{\frac{1}{2}\beta - \frac{1}{2}\sqrt{5}\,\beta}{\beta} & \frac{\frac{1}{2}\beta + \frac{1}{2}\sqrt{5}\,\beta}{\beta} \\ -\frac{-\frac{1}{2}\beta - \frac{1}{2}\sqrt{5}\,\beta}{\beta} & -\frac{-\frac{1}{2}\beta + \frac{1}{2}\sqrt{5}\,\beta}{\beta} & -\frac{\frac{1}{2}\beta - \frac{1}{2}\sqrt{5}\,\beta}{\beta} & -\frac{\frac{1}{2}\beta + \frac{1}{2}\sqrt{5}\,\beta}{\beta} \\ 1 & 1 & 1 & 1 \end{bmatrix}$$

$$Vecs_trans := \left[\begin{array}{cccc}
\frac{1}{\sqrt{2+\frac{2\,\%1^2}{\beta^2}}} & -\frac{\%1}{\sqrt{2+\frac{2\,\%1^2}{\beta^2}}\,\beta} & -\frac{\%1}{\sqrt{2+\frac{2\,\%1^2}{\beta^2}}\,\beta} & \frac{1}{\sqrt{2+\frac{2\,\%1^2}{\beta^2}}} \\
\frac{1}{\sqrt{2+\frac{2\,\%2^2}{\beta^2}}} & -\frac{\%2}{\sqrt{2+\frac{2\,\%2^2}{\beta^2}}\,\beta} & -\frac{\%2}{\sqrt{2+\frac{2\,\%2^2}{\beta^2}}\,\beta} & \frac{1}{\sqrt{2+\frac{2\,\%2^2}{\beta^2}}} \\
-\frac{1}{\sqrt{2+\frac{2\,\%3^2}{\beta^2}}} & \frac{\%3}{\sqrt{2+\frac{2\,\%3^2}{\beta^2}}\,\beta} & -\frac{\%3}{\sqrt{2+\frac{2\,\%3^2}{\beta^2}}\,\beta} & \frac{1}{\sqrt{2+\frac{2\,\%3^2}{\beta^2}}} \\
-\frac{1}{\sqrt{2+\frac{2\,\%4^2}{\beta^2}}} & \frac{\%4}{\sqrt{2+\frac{2\,\%4^2}{\beta^2}}\,\beta} & -\frac{\%4}{\sqrt{2+\frac{2\,\%4^2}{\beta^2}}\,\beta} & \frac{1}{\sqrt{2+\frac{2\,\%4^2}{\beta^2}}}
\end{array}\right]$$

$$\%1 := -\frac{1}{2}\beta - \frac{1}{2}\sqrt{5}\,\beta$$
$$\%2 := -\frac{1}{2}\beta + \frac{1}{2}\sqrt{5}\,\beta$$
$$\%3 := \frac{1}{2}\beta - \frac{1}{2}\sqrt{5}\,\beta$$
$$\%4 := \frac{1}{2}\beta + \frac{1}{2}\sqrt{5}\,\beta$$

$$Result := \left[\begin{array}{c}
\frac{5\,\alpha+5\,\beta+3\,\sqrt{5}\,\beta+\alpha\,\sqrt{5}}{5+\sqrt{5}},\,0,\,0,\,0 \\
0,\,\frac{-5\,\alpha-5\,\beta+3\,\sqrt{5}\,\beta+\alpha\,\sqrt{5}}{-5+\sqrt{5}},\,0,\,0 \\
0,\,0,\,\frac{-5\,\alpha+5\,\beta-3\,\sqrt{5}\,\beta+\alpha\,\sqrt{5}}{-5+\sqrt{5}},\,0 \\
0,\,0,\,0,\,\frac{5\,\alpha-5\,\beta-3\,\sqrt{5}\,\beta+\alpha\,\sqrt{5}}{5+\sqrt{5}}
\end{array}\right]$$

$$\left[\begin{array}{cccc}
\alpha+\frac{(5+3\,\sqrt{5})\,\beta}{5+\sqrt{5}} & 0 & 0 & 0 \\
0 & \alpha+\frac{(-5+3\,\sqrt{5})\,\beta}{-5+\sqrt{5}} & 0 & 0 \\
0 & 0 & \alpha+\frac{(5-3\,\sqrt{5})\,\beta}{-5+\sqrt{5}} & 0 \\
0 & 0 & 0 & \alpha+\frac{(-5-3\,\sqrt{5})\,\beta}{5+\sqrt{5}}
\end{array}\right]$$

Since this output is a little strange, it behooves us to check that it's what we expect.

Consider

$$\frac{1+\sqrt{5}}{2}$$

and multiple top and bottom by $5+\sqrt{5}$, i.e.,

$$\left(\frac{1+\sqrt{5}}{2}\right)\left(\frac{5+\sqrt{5}}{5+\sqrt{5}}\right)$$

which yields

$$\frac{5+6\sqrt{5}+5}{2(5+\sqrt{5})}$$

yielding, ultimately,

$$\frac{1+\sqrt{5}}{2}=\frac{5+3\sqrt{5}}{5+\sqrt{5}}$$

So there!

[1] C. R. Gatz, *Introduction to Quantum Chemistry*, Charles E. Merrill Publishing Co., Columbus, Ohio, 1971, page 290
[2] S. R. La Paglia, *Introductory Quantum Chemistry*, Harper and Row Publishers, New York, 1971, page 305
[3] A. Streitweiser Jr., *Molecular Orbital Theory for Organic Chemists*, John Wiley and Sons, Inc., New York, 1962.