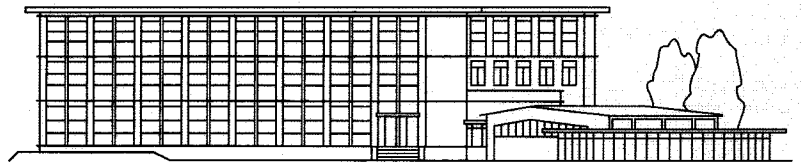




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## Block-Diagonalization of Hermitian Matrices.

Problem: find  $\overset{\text{unitary}}{T}$  such that  $\mathcal{H} = T^+ H T$  has nonzero elements only in blocks along the diagonal

You can do it this way (H is Hermitian)

Step 1: Diagonalize H

Step 2: Apply any ~~block~~ unitary consistent with block structure.

The set of block-consistent unitaries is infinite, so there are infinitely many ways.

However if you impose the condition that T do as little as possible other than block diagonalize H, then there is only one way.

new problem: find T ( $T^+ T = T T^+ = I$ ) such that

$\mathcal{H} = T^+ H T$  is blocked, and  $\|\hat{T} - \hat{I}\| \Rightarrow \text{minimum}$

↑  
Euclidean norm (Frobenius, Hilbert-Schmidt, 2-norm...  
(Actually it doesn't matter as long as it's unitarily invariant))

The answer is

$$T = S S_{BD}^+ (S_{BD} S_{BD}^+)^{-1/2}$$

or equivalently

$$T = U (U^+ U)^{-1/2} \text{ where } U = S S_{BD}^{-1}$$

(where S satisfies

$S_{BD}$  is ~~the~~ S, projected on to blocks

$$\begin{bmatrix} S_{11} & & \\ & S_{22} & \\ & & \dots \end{bmatrix}$$

$H S = S \Lambda$   
ie. columns of S are  
eigenvectors of H

This becomes obvious if you know:

(Asserted)

Theorem: The closest unitary matrix to some <sup>nonsingular</sup> matrix

$$\mathbf{M} \text{ is } \mathbf{M}(\mathbf{M}^+\mathbf{M})^{-1/2} \text{ (acting in column space)}$$

$$\text{or } \mathbf{M}(\mathbf{M}\mathbf{M}^+)^{-1/2} \text{ (acting in row space)}$$

~~For the usual case, these~~ these are equivalent if the row & column spaces are the same.

~~Using the left polar decomposition~~

~~I'm not proving this for you, but it should be clear that this is the same way that a unit vector is made out of a vector. (modified for non-commutative matrix multiplication)~~

. If you accept this, then it is clear what is happening:

$U = S S_{\text{Bo}}^{-1}$  is a diagonalization of ~~S~~ H, followed by an inverse operation restricted to the blocks

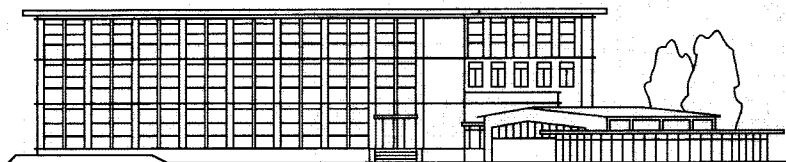
$T = U(U^+U)^{1/2}$  is the closest unitary approximation to U!

The columns of U span the same space as the columns of S (or H) but are disjoint under the operation by H.



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It is worth noting that if the block diagonalization is onto 2 blocks then

$$U = \begin{pmatrix} 1 & X \\ -X^\dagger & 1 \end{pmatrix} \quad \text{where } X = -(S_{21} S_{11}^{-1}) \\ = S_{12} S_{22}^{-1}$$

This powerful result tells you that you only need to know the eigenvectors corresponding to one block of  $H$  in order to compute  $T$ !

~~(this is due to the fact that~~

this is useful practically because if you apply this to a state-averaged CAS-SCF calculation, you only need to use the data for the optimized space. (which is all the non-redundant info. that you have).

(An equivalent development for a Hartree-Fock state would make clear that knowing the occupied states gives you sufficient information to construct the virtual states)

Also, a correlated effective hamiltonian can be built by applying perturbation theory only to the states in the lower block, and using the reference eigenvectors of that block to compute the ~~block~~ transformation

$$R = \frac{S_{BD}^\dagger (S_{BD} S_{BD}^\dagger)^{-1/2}}{\cancel{(S_{BD} S_{BD}^\dagger)}} \quad \text{for only the block of interest}$$

# Application to Quasi-Diabatic States

Molecular Hamiltonian is:

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{U}(r, Q)$$

Nuclear k.E.      Electronic k.E.      Potential  
Nuclear D.O.F.      Electronic D.O.F.

Expand Hilbert space for molecule as:

$$\Psi(r, Q) = \sum_n \chi_n(Q) \Phi_n(r, Q)$$

and plug into Schrödinger Equation:

$$(\hat{H} - E)\Psi(r, Q) = 0$$

gets you

$$(\hat{T}_N \mathbb{1} + \hat{H}_e - E\mathbb{1})\chi = \tilde{\Lambda}\chi$$

$\chi$  is column vector with units  $\chi_n$ ,  $\hat{H}_e$  is "electronic Hamiltonian"

$$(\tilde{H}_e)_{nm} = \langle \Phi_n | \hat{H}_e | \Phi_m \rangle$$

and  $\tilde{\Lambda}$  is the "nonadiabatic coupling matrix"

$$\tilde{\Lambda}_{nm} = \langle \Phi_n | \hat{T}_N | \Phi_m \rangle - \langle \Phi_n | \Phi_m \rangle \hat{T}_n$$

$\uparrow = 0$  if electronic states are chosen orthogonal

You can decompose  ~~$\hat{T}_N$~~   $\hat{T}_N$  as

$$\hat{T}_N = -\frac{1}{\sqrt{g}} \frac{\partial}{\partial Q_i} \sqrt{g} g^{ij} \frac{\partial}{\partial Q_j} \quad (\text{Einstein Abomination Summation})$$

in general curvilinear coordinates  $Q$

For many problems, the couplings represented by  $A$  are only large in a subset of electronic states.

One might hope to use a diabatic basis such that the ~~couplings~~ couplings vanish. This is generally impossible without access to the full electronic basis.

more formally, one wants

$$\phi_\alpha = A_{\alpha'\alpha}(Q) \Phi_{\alpha'} \text{ such that}$$

$$A^\dagger F_{\alpha\alpha}^{(i)} A + A^\dagger \frac{\partial}{\partial Q_i} A = 0$$

giving an equation for  $A$ :

$$F_{\alpha\alpha}^{(i)} A + \frac{\partial}{\partial Q_i} A = 0$$

This is generally insoluble for anything more complex than a diatomic molecule, unless the full electronic basis is used.

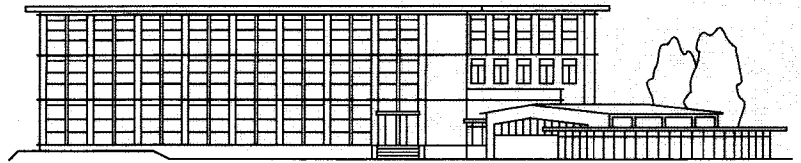
To see this point, note that a "crude adiabatic" basis  $\psi^0$  can be defined by freezing the electronic states at some geometry and then using this basis for all geometries. Then the nonadiabatic couplings are zero by construction, but the number of  $\psi^0$  needed to describe the electronic state will rise very fast as the geometry is changed.  
("least action")

The block diagonalization transform can be used to produce a quasi-diabatic few-state Hamiltonian for the electrons given a reference space (not necessarily block diagonal) that is already quasi-diabatic.



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To see how this would be useful for the  $\{\Phi_n\} = \{\Psi_n^0\}$   
"crude adiabatic" case  $F^{(i)} = 0$

then intrablock couplings are  $F_{dd}^{ad(i)} = S_{dd}^+ S_{dd,i} + S_{\beta d}^+ S_{\beta d,i}$   
(in block  $d$  of adiabatic basis)

where  $S_{dd,i} = \frac{d}{dq_i} S_{dd}$

then

$$F^{ad(i)} = S_{dd}^{-1} S_{dd,i} + S_{dd}^+ X X_{ii}^+ S_{dd}^-$$

now  $X X_{ii}^+ = -P_{dd}^{-1} P_{dd,i} P_{dd}^{-2} - P_{dd}^{-2} P_{dd,i} P_{dd}^{-1} - X_{ii} X^+$

where  $P_{dd} = (S_{dd} S_{dd}^+)^{1/2} = (1 + X X^+)^{-1/2}$

now  $F^{ad(i)} = W_{dd}^{ad(i)} + N_{dd}^{ad(i)}$

$$W_{dd}^{ad(i)} = S_{dd}^{-1} S_{dd,i} - S_{dd}^{-1} P_{dd,i} P_{dd}^{-1} S_{dd}$$

information from  $d$  block only

$$N_{dd}^{ad(i)} = -S_{dd}^+ P_{dd}^{-1} P_{dd,i} (S_{dd}^+)^{-1} - S_{dd}^+ X_{ii} X^+ S_{dd}$$

from coupling to  $\beta$  block  
via  $X$

now transform to quasi adiabatic basis

$$F_{dd}^{qd(i)} = R_{dd}^+ F_{dd}^{ad(i)} R_{dd} + R_{dd}^+ R_{dd,i} \quad R_{dd} = S_{dd}^{-1} P_{dd}$$

$$R_{dd}^+ R_{dd,i} = -P_{dd}^{-1} S_{dd,i} S_{dd}^{-1} P_{dd} + P_{dd}^{-1} P_{dd,i}$$

so  $W_{dd}^{qd(i)} = R_{dd}^+ W_{dd}^{ad(i)} R_{dd} = P_{dd}^{-1} S_{dd,i} S_{dd}^{-1} P_{dd} - P_{dd}^{-1} P_{dd,i}$

$$N_{dd}^{qd(i)} = R_{dd}^+ N_{dd}^{ad(i)} R_{dd} = -P_{dd,i} P_{dd}^{-1} - P_{dd} X_{ii} X^+ P_{dd}$$

from which we see

$$F_{dd}^{qd(i)} = N_{dd}^{ad(i)}$$

Which shows that the effect of the block diagonalization has been to transform away  $W_{dd}^{ad(i)}$ !

Since  $N_{dd}^{ad(i)}$  contains information about the decoupling of  $\alpha$  and  $\beta$ , we know that this arises solely from the BD Transformation itself, which is not surprising (because  $F=0$  in the reference basis)

For an arbitrary reference basis  $F \neq 0$

$$\text{then } F^{ad(i)} = S^+ F^{(i)} S + S^+ S_{,i}$$

$$\text{and } F^{qd(i)} = T^+ F^{(i)} T + T^+ T_{,i}$$

the intra block couplings are

$$F_{dd}^{ad(i)} = W_{dd}^{ad(i)} + N_{dd}^{ad(i)} + E_{dd}^{ad(i)}$$

$$E_{dd}^{ad(i)} = S_{dd}^+ F_{dd}^{(i)} S_{dd} + S_{\beta d}^+ F_{\beta d}^{(i)} S_{dd} + S_{dd}^+ F_{\alpha \beta}^{(i)} S_{\beta d} + S_{\beta d}^+ F_{\beta \beta}^{(i)} S_{\beta d}$$

This decomposition shows that  $W$  is also transformed away in the general case for any initial basis

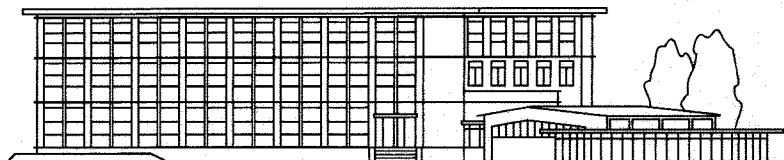
$$F_{dd}^{qd(i)} = (P_{dd} X X_{,i}^+ - P_{dd,i}^{-1}) P_{dd} + E_{dd}^{qd(i)}$$

$$E_{dd}^{qd(i)} = R_{dd}^+ E_{dd}^{qd(i)} R_{dd} = P_{dd} (F_{dd}^{(i)} - X F_{\beta d}^{(i)} - F_{\alpha \beta}^{(i)} X^+ + X F_{\beta \beta}^{(i)} X^+) P_{dd}$$



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$W$  is always transformed away because  $T$  is uniquely determined by  $S$

$W$  has no rotational part. In general, only the irrotational part of the NA coupling can be transformed away.

(this is because only vector fields with zero curl can be represented as the gradient of a scalar potential)

$W$  may not be all of the irrotational part of  $F$

In order for all of this to be useful, we need two

Conditions:

1.  $F$  should be already small in reference basis (i.e. it should be quasi-adiabatic)
2.  $X$  should be small and depend weakly on the nuclear coordinates

For the inter-block couplings:

$$F_{\alpha\beta}^{ad(i)} = P_{\alpha\alpha} X_{,i} P_{\beta\beta} + E_{\alpha\beta}^{ad(i)}$$

$$E_{\alpha\beta}^{ad(i)} = P_{\alpha\alpha} (F_{\alpha\beta}^{(i)} + F_{\alpha\alpha}^{(i)} X_{,i} + F_{\beta\beta}^{(i)} X_{,i} + F_{\beta\alpha}^{(i)} X_{,i}) P_{\beta\beta}$$

we see that these will be small if the same conditions hold.



