Quantum Chemistry 2023, MOL406, week 3

November 22, 2023

Unitary operator (here called \hat{U}):

$$\hat{U}^{\dagger}\hat{U}=\hat{U}\hat{U}^{\dagger}=\hat{I}$$
 i.e. $\hat{U}^{-1}=\hat{U}^{\dagger}$

So the adjoint is the inverse.

Remember the definition of the adjoint operator \hat{U}^{\dagger} :

$$\langle \hat{U}\psi_1, \psi_2 \rangle = \langle \psi_1, \hat{U}^{\dagger}\psi_2 \rangle$$

A unitary *matrix* (here called **U**):

$$\mathbf{U}^{\dagger}\mathbf{U} = \mathbf{U}\mathbf{U}^{\dagger} = \mathbf{1}$$
 i.e. $\mathbf{U}^{-1} = \mathbf{U}^{\dagger}$

To get the "Hermitian adjoint" matrix \mathbf{U}^{\dagger} :

$$U_{ij}^{\dagger}=U_{ji}^{*}$$

Important properties:

 $|\det(U)|=1~$ and $~U=V\tilde{U}V^{\dagger}~$ where \tilde{U} is diagonal and $\tilde{V}^{(\dagger)}$ and \tilde{U} unitary

Hermitian operator (here called \hat{H}):

$$\hat{H}=\hat{H}^{\dagger}$$

It is self-adjoint.

$$\langle \hat{H}\psi_1,\psi_2
angle=\langle\psi_1,\hat{H}\psi_2
angle$$

For an Hermitian matrix \mathbf{H} :

$$H_{ij}^{\dagger}=H_{ji}^{*}=H_{ij}$$

It can be diagonalized with a unitary matrix and has real eigenvalues. The determinant (the product of the eigenvalues) is real.

For square matrices:

 $det(\mathbf{AB}) = det(\mathbf{A}) det(\mathbf{B})$

Let's rotate the orbitals with a unitary matrix **U**:

$$\sum_{\lambda} \chi_{\lambda} \mathbf{C}'_{\lambda k} = \phi'_{k} = \sum_{l} \phi_{l} \mathbf{U}_{lk} = \sum_{l} \sum_{\mu} \chi_{\mu} \mathbf{C}_{\mu l} \mathbf{U}_{lk} = \sum_{\lambda} \chi_{\lambda} \sum_{l} \mathbf{C}_{\lambda l} \mathbf{U}_{lk}$$

We did this such that evidently: $\mathbf{C}' = \mathbf{C}\mathbf{U} \Rightarrow \mathbf{C} = \mathbf{C}'\mathbf{U}^{\dagger}$.

We can go back to the spinorbitals ψ_i and, in our restricted closed shell HF, get a block diagonal **V** that transforms the spin orbitals (one block for the α , the other for the β spin):

$$\mathbf{V} = \left(\begin{array}{cc} \mathbf{U} & \mathbf{0} \\ \mathbf{0} & \mathbf{U} \end{array} \right)$$

Because the determinant of the product is the product of the determinants

$$\Phi' = \frac{1}{\sqrt{N!}} \det \left| \psi_1'(1) \psi_2'(2) \dots \psi_N'(N) \right| = \frac{1}{\sqrt{N!}} \det \left| \psi_1(1) \psi_2(2) \dots \psi_N(N) \right| \det(\mathbf{V}) = \Phi \det(\mathbf{V})$$

So $\Phi' = \pm \Phi$, well... $\Phi' = \Phi e^{i\tilde{\phi}}$. The fase factors cancel in any expectation value, i.e. *chemisty & physics are unaffected*. So also our HF energy is not affected.

Remember:

$$P_{\mu\lambda} = \sum_{k}^{N/2} C_{\mu k} C_{\lambda k}^* = \sum_{k}^{N/2} C_{\mu k} C_{k\lambda}^{\dagger} \text{ i.e. } \mathbf{P} = \mathbf{C} \mathbf{C}^{\dagger}$$

Transform the density matrix:

$$\mathbf{P}' = \mathbf{C}'\mathbf{C}'^\dagger = \mathbf{C}\mathbf{U}(\mathbf{C}\mathbf{U})^\dagger = \mathbf{C}\mathbf{U}\mathbf{U}^\dagger\mathbf{C}^\dagger = \mathbf{P} \Rightarrow \mathbf{F}' = \mathbf{F}$$

So the Fock matrix is unaffected (as is **S**).

 $2FC = SC\Lambda$ $2FC'U^{\dagger} = SC'U^{\dagger}\Lambda$ $2F'C'U^{\dagger} = S'C'U^{\dagger}\Lambda$ $2F'C' = S'C'U^{\dagger}\Lambda = S'C'\Lambda'$

We can always choose **U** such that it diagonalizes Λ (i.e. Λ' is diagonal) because the latter is hermitian (**U** is unitary, Λ is hermitian).

Write (now Λ denotes the diagonal matrix):

$$\mathbf{\Lambda} \equiv 2\boldsymbol{\epsilon} = 2 \begin{pmatrix} \epsilon_1 & 0 & \dots & 0 \\ 0 & \epsilon_2 & \dots & 0 \\ \vdots & \vdots & & \vdots \\ 0 & 0 & \dots & \epsilon_{N/2} \end{pmatrix}$$

so that we obtain the Roothaan equations:

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\epsilon} \ , \ \mathbf{C} = \begin{pmatrix} c_{11} & c_{12} & \dots & c_{1N/2} \\ c_{21} & c_{22} & \dots & c_{2N/2} \\ \vdots & \vdots & & \vdots \\ c_{M1} & c_{M2} & \dots & c_{MN/2} \end{pmatrix}$$

We can write it for the columns of **C** separately:

$$\mathbf{F}_{\mathbf{C}_{k}} = \epsilon_{k} \mathbf{S}_{\mathbf{C}_{k}} \text{ because } \mathbf{C}_{\boldsymbol{\epsilon}} = \begin{pmatrix} \epsilon_{1}c_{11} & \dots & \epsilon_{k}c_{1k} & \dots & \epsilon_{N/2}c_{1N/2} \\ \vdots & & \vdots & & \vdots \\ \epsilon_{1}c_{M1} & \dots & \epsilon_{k}c_{Mk} & \dots & \epsilon_{N/2}c_{MN/2} \end{pmatrix}$$

This is a generalized eigenvalue problem with eigenvalues ϵ_k and eigenvectors \mathbf{c}_k and overlap matrix \mathbf{S} .

Help slide:

A standard eigenvalue problem (**A** is a matrix, **v** is a vector):

 $\mathbf{A}\mathbf{v} = \lambda\mathbf{v}$

To find the possible eigenvalues λ :

 $\det(\boldsymbol{\mathsf{A}}-\lambda\boldsymbol{\mathsf{I}})=0$

A generalized eigenvalue problem (A and B are matrices, v is a vector):

 $\mathbf{A}\mathbf{v}=\lambda\mathbf{B}\mathbf{v}$

To find the possible eigenvalues λ :

$$\det(\mathbf{A} - \lambda \mathbf{B}) = 0$$

Let's remember how the Fock matrix was defined

Relabel and expand density matrix and obtain MOs:

$$F_{\lambda\mu} = h_{\lambda\mu} + \sum_{\nu\tau} P_{\tau\nu} \langle \lambda\nu | (2 - \hat{P}_{12})\hat{g} | \mu\tau \rangle \text{ where}$$

$$P_{\tau\nu} = \sum_{k}^{N/2} C_{\tau k} C_{\nu k}^* \text{ and } \phi_k^* = \sum_{\nu}^{M} \chi_{\nu}^* C_{\nu k}^* \text{ and } \phi_k = \sum_{\tau}^{M} \chi_{\tau} C_{\tau k}$$

$$\langle \chi_{\lambda} | \hat{f} | \chi_{\mu} \rangle \equiv F_{\lambda\mu} = h_{\lambda\mu} + \sum_{\nu\tau} \sum_{k}^{N/2} C_{\tau k} C_{\nu k}^* \langle \lambda\nu | (2 - \hat{P}_{12})\hat{g} | \mu\tau \rangle$$

$$= h_{\lambda\mu} + \sum_{k}^{N/2} \langle \chi_{\lambda} \phi_k | (2 - \hat{P}_{12})\hat{g} | \chi_{\mu} \phi_k \rangle$$

$$\begin{split} &\langle \chi_{\lambda}(1)|\hat{f}(1)|\chi_{\mu}(1)\rangle = \langle \chi_{\lambda}(1)|\hat{h}(1)|\chi_{\mu}(1)\rangle \\ &+ 2\sum_{k}^{N/2} \langle \chi_{\lambda}(1)\phi_{k}(2)|\hat{g}(1,2)|\chi_{\mu}(1)\phi_{k}(2)\rangle - \sum_{k}^{N/2} \langle \chi_{\lambda}(1)\phi_{k}(2)|\hat{P}_{12}\hat{g}(1,2)|\chi_{\mu}(1)\phi_{k}(2)\rangle \end{split}$$

We carry out the integration over the second space coordinate and lump it together with the colored parts. We see \hat{f} is a one-electron operator. It is *the same* operator for all electrons (because we have *cancelling self-exchange and self-Coulomb terms*). All electrons feel the mean field of all the electrons. There is no electron correlation.

$$\hat{f}(1) = \hat{h}(1) + \sum_{k=1}^{N/2} \left(2\hat{J}_k(1) - \hat{K}_k(1) \right) \quad ,$$

 $\hat{J}_k(1) \equiv \int d\mathbf{r}_2 rac{\phi_k^*(2)\phi_k(2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad , \quad \hat{K}_k(1) \equiv \int d\mathbf{r}_2 rac{\phi_k^*(2)\hat{P}_{12}\phi_k(2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$

The eigenvalue problem can be written as the HF equation:

 $\hat{f}(1)\phi_k(1) = \epsilon_k\phi_k(1)$

In a basis this boils down to the Roothaan equations, just expand:

$$\hat{f}(1)\sum_{\lambda}\chi_{\lambda}C_{\lambda k}=\sum_{\lambda}\chi_{\lambda}C_{\lambda k}\epsilon_{k}$$

Take the inner product with $|\chi_{\mu}\rangle$ from the left:

$$\sum_{\lambda} F_{\mu\lambda} C_{\lambda k} = \sum_{\lambda} \langle \chi_{\mu} | \hat{f}(1) | \chi_{\lambda} \rangle C_{\lambda k} = \sum_{\lambda} \langle \chi_{\mu} | \chi_{\lambda} \rangle C_{\lambda k} \epsilon_{k} = \sum_{\lambda} S_{\mu\lambda} C_{\lambda k} \epsilon_{k} ,$$

i.e. $\mathbf{Fc}_{k} = \epsilon_{k} \mathbf{Sc}_{k}$

With the diagonal matrix of Lagrange multipliers $\epsilon = \Lambda/2$, this can be written:

$$\sum_{\lambda} F_{\mu\lambda} C_{\lambda k} = \sum_{\lambda} \langle \chi_{\mu} | \chi_{\lambda} \rangle C_{\lambda k} \epsilon_{k} = \sum_{\lambda} \sum_{\tilde{k}} S_{\mu\lambda} C_{\lambda \tilde{k}} \Lambda_{\tilde{k} k} / 2 ,$$

i.e. $\mathbf{FC} = \mathbf{SC} \epsilon$ (Roothaan)

Towards Hartree-Fock: Solving

The Roothaan equations can be solved on a computer. It is a generalized eigenvalue problem, i.e. linear algebra. It can be solved with a LAPACK call. Input: the Fock and overlap matrices. Output: the eigenvector matrix **C** and the eigenvalues ϵ_k .

Remember: The Fock matrix has greek indices only $(F_{\rho\mu})$. Its size, $M \times M$, is defined by the basis (there are M basis functions). The same holds for the overlap matrix **S**. Matrix **C** has dimensions $M \times N/2$... but the computer will give M eigenvectors with their eigenvectors, i.e. return an $M \times M$ matrix for **C**. The lowest N/2 eigenvalues are with the occupied states (our matrix **C** in the HF derivation). So M should be at least N/2. In practise M > N/2 and we also get empty, virtual states (LUMO and higher).

The story isn't complete \ldots The Fock matrix depends on the density matrix, i.e. on the eigenvector matrix \mathbf{C} .

Towards Hartree-Fock: Solving

The story isn't complete \ldots The Fock matrix depends on the density matrix, i.e. on the eigenvector matrix \mathbf{C} .

So the Roothaan equations are only solved if the output of the diagonalisation yields the same eigenvectors (within a unitary transformation) as were used to build the Fock matrix ... the solution needs to be *self-consistent*.

To attain self-consistency, in principle, one runs trough a repeated cycle:

guess $\mathbf{C} \rightarrow \text{build } \mathbf{F} \rightarrow \text{solve for } \mathbf{C} \text{ and } \epsilon_k \rightarrow \text{build } \mathbf{F} \rightarrow \text{etc.}$

This is a feedback system: care is needed mixing input & output (density) matrices to yield stable and "rapid" convergence (instead of divergence). In solids this can be more tricky than in molecules.

Towards Hartree-Fock: the eigenvalues

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Once we have the converged orbitals, inserting in h_{kk} , etc., yields the (ground state) energy of our system:

$$E = \epsilon = \langle \Psi | \hat{H} | \Psi \rangle = \sum_{k}^{N/2} 2h_{kk} + \sum_{k}^{N/2} \sum_{l}^{N/2} (2J_{kl} - K_{kl})$$

We also have the eigenvalues. Per eigenvalue we have an α and a β spin. We can add:

$$\tilde{\epsilon} \equiv \sum_{k}^{N/2} 2\epsilon_k \neq \epsilon$$

To see why,

$$\langle \phi_{k}(1)|\hat{f}(1)\phi_{k}(1)\rangle = \langle \phi_{k}(1)| \left[\hat{h}(1) + \sum_{l=1}^{N/2} \left(2\hat{J}_{l}(1) - \hat{K}_{l}(1)\right)\right] \phi_{k}(1)\rangle = \langle \phi_{k}(1)|\epsilon_{k}\phi_{k}(1)\rangle = \epsilon_{k} \Rightarrow$$

$$= 2\sum_{k}^{N/2} \langle \phi_{k}(1)|\hat{f}(1)|\phi_{k}(1)\rangle = 2\sum_{k}^{N/2} \left\{ \langle \phi_{k}(1)|\hat{h}(1)|\phi_{k}(1)\rangle + \sum_{l=1}^{N/2} \left(2\langle \phi_{k}(1)|\hat{J}_{l}(1)|\phi_{k}(1)\rangle - \langle \phi_{k}(1)|\hat{K}_{l}(1)|\phi_{k}(1)\rangle\right) \right\}$$
hence: $\epsilon = \tilde{\epsilon} - \sum_{k}^{N/2} \sum_{l=1}^{N/2} \left(2J_{kl} - K_{kl}\right)$ Double counting!

This comes from the minimization where the derivative w.r.t. $C_{\rho m}^*$ was taken (week 2). The 2-electron term depends on a product of density matrices, yielding the same contribution twice.

Towards Hartree-Fock: the eigenvalues

Help slide:

$$\frac{\partial}{\partial C_{\rho m}^{*}} \left(\sum_{\lambda \mu \nu \tau} \mathcal{P}_{\nu \lambda} \mathcal{P}_{\tau \mu} \langle \lambda \mu | (2 - \hat{\mathcal{P}}_{12}) \hat{g} | \nu \tau \rangle \right) = 2 \sum_{\nu} \sum_{\mu \tau} \mathcal{P}_{\tau \mu} \langle \rho \mu | (2 - \hat{\mathcal{P}}_{12}) \hat{g} | \nu \tau \rangle C_{\nu m}$$

Towards Hartree-Fock: the eigenvalues

Remember: if M > N/2 diagonalization of the Roothaan problem will also yield unoccupied orbitals and eigenvalues.

Koopmans' theorem

We remove an electron *i* from the system and assume that the orbitals are *unaffected*. Subtracting the HF energies of both systems, we find an expression (previous slide) exactly equal to the orbital eigenvalue ϵ_i . Hence, if ϵ_i is in the HOMO eigenvalue:

$IP = -\epsilon_i$

I.e., the ionization potential is minus the HOMO eigenvalue. This is Koopman's theorem. One can also add an electron to a virtual orbital v. For the LUMO:

$$\mathsf{E}\mathsf{A} = -\epsilon_{\mathsf{A}}$$

EA is the electron affinity. Both IP and EA are positive.

Note: we neglect relaxation of the depleted state... i.e. the calculated IP is too large. However, we also neglect electron correlation, which works the other way, making Koopman's IP often a reasonable number.

The ϵ_v (of neutral molecules) are often positive in HF, yielding unphysical negative EA. The HOMO-LUMO gap in HF is often (much) too large.

Our MOs $|\phi_k\rangle$ are linear combinations of atom-centred basis functions $\chi_{\lambda}(\mathbf{r})$:

$$\phi_k(\mathbf{r}) = \sum_{\lambda}^M C_{\lambda k} \chi_{\lambda}(\mathbf{r})$$

The sum is a double sum: it runs over all atoms and over all the orbitals belonging to the atoms. This is common practise in most molecular quantum chemical programs (other choices for $\chi_{\lambda}(\mathbf{r})$ are possible).

Slater type orbitals (STOs):

$$\chi(\mathbf{r}) = r^{n-1} e^{-\zeta r} Y_{lm}(\theta, \phi)$$

 $(n \sim \text{principal quantum number})$

E.g., the 1s in hydrogen with nucleus sitting at **R**:

$$\phi_{1s}(\mathbf{r}-\mathbf{R})=\sqrt{\zeta^3/\pi}\,e^{-\zeta|\mathbf{r}-\mathbf{R}|}$$

Note that $d\phi_{1s}/dr \neq 0$ at $r = |\mathbf{r} - \mathbf{R}| = 0$. Cusp!

Slater type orbitals are very suitable to quantum chemical problems, but computationally awkward. Most chemists use Gaussians. You can use them to approxmate STOs.

A general Gaussian type orbital (GTO), Cartesian:

$$\eta(\mathbf{r};\alpha_i) = x^l y^m z^n e^{-\alpha_i r^2}$$

▶
$$l + m + n = 0$$
, i.e. $l = m = n = 0$ gives an *s*-orbital

▶ l + m + n = 1, i.e. n = 1 or m = 1, or l = 1 gives the 3 *p*-orbitals

I + m + n = 2, gives x², xy, y², yz, z² or xz. These are proportional to linear combinations of the 5 (angular) d-functions: d_{xy}, d_{yz}, d_{zx}, d_{x²-y²} and d_{3z²-r²}, who, in turn, are a linear mix of the five spherical harmonics Y_{2m}, with m = −2,...,2. There is one additional combination: x² + y² + z² = r² that yields and extra function of s symmetry.

STO minimal basis sets: the minimum number of STOs needed to accommodate all electrons, e.g. C: 1s, 2s and 2p: 1 + 1 + 3 = 5 STOs.

Optimizing the coefficients (the "zeta"s, i.e. " ζ "s) in a series of HF calculations on the atom \rightarrow "energy-optimized single-zeta STO basis".

Approximate the STOs as a sum of Gaussians with (optimized) coefficients:

$$\mathsf{STO} = \sum_{i=1}^{L} d_i \eta(\mathbf{r}; lpha_i)$$

Fix the d_i (called "contraction") and α_i in subsequent molecular calculations. If, e.g., L = 4, we have a STO-4G basis.

So the STO-4G basis gives a small set of *element-specific* exponents and contraction coefficients.

Gaussian basis sets (Pople). Consider, e.g., for C:

SV 4-31G

- "4" the 1s is a contraction of 4 Gaussians ("G"). A single basis function. For a general element: each core state is a contraction of 4 Gs.
- ▶ "SV" we have "split valence", i.e. two (radial) basis functions for the valence 2s and 2p.
- "31" tells us how the valence is split: One contraction of 3 Gaussians, and one of a single Gaussian. So for 2s we get 2 basis functions, for 2p we get 6. One calls this "double zeta". One can add, e.g. "SV 6-311" is "triple zeta". More variational freedom!
- Pople cs did not base their basis functions on STOs, but optimized their contraction coefficients and exponents directly on the atom.
- We need many GTOs to approximate the cusp in the 1s. An "SV 6-31G" is better in this respect. A contraction of 6 functions mimics the 1s.
- SV 4-31G* We can add "polarization functions", i.e. AOs with *I* quantum number of the first "empty shell", so in this case *d* functions. To add also on hydrogen: SV 4-31G**
- SV 4-31+G has diffusive functions added. With SV 4-31++G also for hydrogen.