

Lecture on Fundamental models of quantum chemistry

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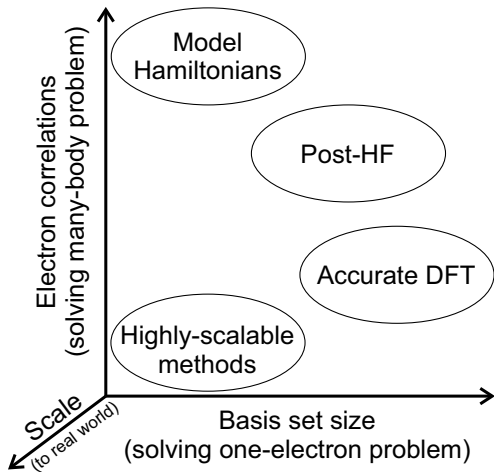
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Outline

- Introduction
- 2c2e model of chemical bond
- 3c4e model of hypervalent and secondary bonding
- 4c4e dimer model of dispersion force, solvatochromism
- onsite 2c2e model for Hund's rule and orbital relaxation
- onsite 3c3e model of atomic levels
- 4c4e tetrahedral model of metals and static correlations
- 4c4e ring model of density waves
- 1D extended Hubbard model
- 1D Peierls model (SSH model)

Goals

The goal of this lecture is to demonstrate key concepts of quantum chemistry using the simplest possible models



Considered models

- One-electron models – well covered elsewhere
- Electron-electron interaction models – in focus
- Electron-phonon models – in brief

Considered electron-electron models

$$H = \sum_{i,k=1}^L \sum_{\sigma}^{\uparrow\downarrow} c_{i\sigma}^{\dagger} H_{ik}^{1e} c_{k\sigma} + \frac{1}{2} \sum_{i,j,k,l=1}^L \sum_{\sigma\tau}^{\uparrow\downarrow} c_{i\sigma}^{\dagger} c_{j\tau}^{\dagger} W_{ijkl} c_{l\tau} c_{k\sigma}$$

- Onsite models
 - ▶ *LoNe* model – N electrons on L orbitals
 - ▶ All W_{ijkl} are large but linearly dependent due to symmetry
 - ▶ Any molecule in MO basis
- One orbital per site models
 - ▶ *LcNe* model – N electrons on L centers
 - ▶ Most of W_{ijkl} are small enough to be neglected
 - ▶ Include infinite systems \implies quantum phase transitions
- Semiempirical Hamiltonians
 - ▶ PM7 in MOPAC program
 - ▶ Well parameterized for real molecules and solids
 - ▶ Perfect for self-training

Onsite models

$$H = \sum_{i=1}^L \varepsilon_i n_i + \frac{1}{2} \sum_{i,j,k,l=1}^L \sum_{\sigma\tau}^{\uparrow\downarrow} c_{i\sigma}^+ c_{j\tau}^+ W_{ijkl} c_{l\tau} c_{k\sigma}$$

Parameters (below $i \neq j \neq k \neq l$, "site" = basis set orbital):

- $\varepsilon_i = H_{ii}^{1e}$ – orbital energy per shell ($s, p, d; \sigma, \delta; e_g, t_{2u}$)
- onsite Coulomb repulsion $U_i = W_{iiii}$
- intersite repulsion $V_{ij} = W_{ijij} = \iint \frac{|\varphi_i(x)|^2 \cdot |\varphi_j(y)|^2}{|x-y|} dx dy$
- exchange $X_{ij} = W_{ijij} \equiv W_{jiji} = \iint \frac{\varphi_i(x)\varphi_j(x) \cdot \varphi_i(y)\varphi_j(y)}{|x-y|} dx dy$
- three- and two-center integrals with single intersite overlap
 $v_{ikj} = W_{ijkk} = \iint \frac{\varphi_i(x)\varphi_j(x) \cdot |\varphi_k(y)|^2}{|x-y|} dx dy$
- three-center exchange integral
 $x_{ikj} = W_{ikkj} = \iint \frac{\varphi_i(x)\varphi_k(x) \cdot \varphi_j(y)\varphi_k(y)}{|x-y|} dx dy$
- four-center integrals $w_{ijkl} = \iint \frac{\varphi_i(x)\varphi_k(x) \cdot \varphi_j(y)\varphi_l(y)}{|x-y|} dx dy$

Onsite models: symmetry considerations

Spherical symmetry:

- Single set of l -orbitals – $l + 1$ parameters
- For example, p -orbitals: $U, V, X = \frac{U-V}{2}$
- d -orbitals: 18 different matrix elements but only 3 parameters
- sp -orbitals: $U_{ss}, U_{pp}, V_{sp}, V_{pp}, X_{sp}, X_{pp} = \frac{U_{pp}-V_{pp}}{2}$

Rotational symmetry:

- Doubly degenerate orbitals with $X = \frac{U-V}{2}$

One orbital per site models

Extended Hubbard model:

$$H = \sum_i \varepsilon_i n_i + \sum_{i<j} t_{ij} T_{ij} + \sum_i U_i n_i^\uparrow n_i^\downarrow + \sum_{i<j} V_{ij} n_i n_j + \sum_{i<j} X_{ij} \left(T_{ij}^\uparrow T_{ij}^\downarrow - \sum_\sigma n_i^\sigma n_j^\sigma \right)$$

where $n_i^\sigma = c_{i\sigma}^\dagger c_{i\sigma}$, $n_i = n_i^\uparrow + n_i^\downarrow$, $T_{ij}^\sigma = c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma}$

Parameters (below $i \neq j$):

- $\varepsilon_i = H_{ii}^{1e}$ – onsite energy
- $t_{ij} = H_{ij}^{1e}$ – transfer integral
- $U_i = W_{iiii}$ – onsite repulsion (Hubbard model)
- $V_{ij} = W_{ijij}$ – intersite repulsion (extended Hubbard model)
- $X_{ij} = W_{ijij}$ – exchange integral (uncommon extension)

In most cases V cannot be neglected.

X is small but sometimes important:

$$-\frac{1}{2} \sum_{i<j} X_{ij} n_i n_j - 2 \sum_{i<j} X_{ij} \mathbf{s}_i \cdot \mathbf{s}_j + \frac{1}{2} \sum_{i \neq j} \sum_{\sigma \neq \tau} X_{ij} c_{i\sigma}^\dagger c_{i\tau}^\dagger c_{j\tau} c_{j\sigma}$$

Where are electronic correlations?

Matrix elements of 1e and 2e density matrices:

$$\rho_{ki}^{\sigma} = \langle \Psi | c_{i\sigma}^{\dagger} c_{k\sigma} | \Psi \rangle, \quad \rho_{kij}^{\sigma\tau} = \langle \Psi | c_{i\sigma}^{\dagger} c_{j\tau}^{\dagger} c_{l\tau} c_{k\sigma} | \Psi \rangle$$

For Slater determinant

$$\rho_{kij}^{\sigma\tau} = \rho_{ki}^{\sigma} \rho_{lj}^{\tau} - \delta_{\sigma\tau} \rho_{kj}^{\sigma} \rho_{li}^{\sigma}$$

Simplest correlation function (zero for a single Slater determinant)

$$C_{ij}^{\sigma\tau} = \langle n_i^{\sigma} n_j^{\tau} \rangle - \rho_{ii}^{\sigma} \rho_{jj}^{\tau} + \delta^{\sigma\tau} (\rho_{ij}^{\sigma})^2$$

Correlation energy

$$\frac{1}{2} \sum_{ijkl} \sum_{\sigma\tau} W_{ikjl} \delta \rho_{kij}^{\sigma\tau}$$

Even if $\delta \rho$ is small, W_{ikjl} are large and there are many of them

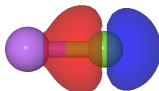
Methods

- Symbolic and numeric exact diagonalization with `ExactDiag` package for **Maple users**, including explicit consideration of spin and symmetries, support of non-abelian groups
- Exact diagonalization and DMRG with ALPS or other programs (QuSpin, TeNPy)
- Post-HF with MOPAC
- Post-HF with Gaussian or other programs (MolPro, NWChem, Q-Chem, Columbus)

Questions

1. When W_{ijkl} have spin indices and when have not?
2. Why intersite exchange integral is small?
3. How to prove that $X = \frac{U-V}{2}$ for rotational symmetry (idea only)?
4. Why for spherical symmetry most of W_{ijkl} are linearly dependent (idea only)?
5. Which terms in H facilitate ferromagnetic or antiferromagnetic ordering?
6. Why abelian symmetries are much simpler to treat in quantum mechanics than non-abelian?

2c2e model of chemical bond



Nonpolar H_2 molecule or polar LiF molecule

- Can be explained using one-electron models
 - ▶ Bonding mechanism and energy
 - ▶ Why excitation breaks the bond (antibonding orbital)
 - ▶ Why electron density is displaced in polar bonds
- Can be explained using electron-electron interaction models
 - ▶ Why triplet excitation is lower than singlet
 - ▶ What are “optical signatures” of e-e correlations
 - ▶ Why DFT is inaccurate at large interatomic distances
 - ▶ Why tight binding is accurate at bonding distances

2c2e model: basis and Hamiltonian

One-electron basis consists of two orbitals φ_1 and φ_2 centered on the 1st and 2nd atoms forming a chemical bond. Let $s = \langle \varphi_1 | \varphi_2 \rangle$. The one-electron overlap and Hamiltonian

$$S^{1e} = \begin{pmatrix} 1 & s \\ s & 1 \end{pmatrix}, \quad H^{1e} = \begin{pmatrix} \varepsilon_1^0 & t_{12}^0 \\ t_{12}^0 & \varepsilon_2^0 \end{pmatrix}$$

Many-body basis for $N = 2$ and $S_z = 0$ consists of 4 functions:

$$|1_1\rangle, \quad |1_2\rangle, \quad |2_1\rangle, \quad |2_2\rangle$$

The overlap matrix for this basis is

$$\begin{pmatrix} 1 & s & s & s^2 \\ \dots & 1 & s^2 & s \\ \dots & \dots & 1 & s \\ \dots & \dots & \dots & 1 \end{pmatrix}$$

Concept: Most of W_{ikjl} can be safely neglected

(while overlaps are important)

Yes, the Hamiltonian

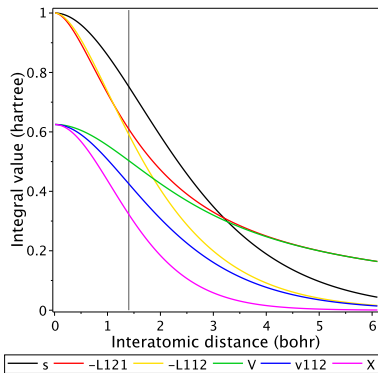
$$H = \begin{pmatrix} 2\varepsilon_1^0 + U_1^0 & s\varepsilon_1^0 + t_{12}^0 + v_{112} & s\varepsilon_1^0 + t_{12}^0 + v_{112} & 2st_{12}^0 + X_{12} \\ \dots & \varepsilon_1^0 + \varepsilon_2^0 + V_{12}^0 & 2st_{12}^0 + X_{12} & s\varepsilon_2^0 + t_{12}^0 + v_{122} \\ \dots & \dots & \varepsilon_1^0 + \varepsilon_2^0 + V_{12}^0 & s\varepsilon_2^0 + t_{12}^0 + v_{122} \\ \dots & \dots & \dots & 2\varepsilon_2^0 + U_2^0 \end{pmatrix}$$

can be written in UV-representation (or zero differential overlap):

$$H = \begin{pmatrix} 2\varepsilon_1 + U_1 & s\varepsilon_1 + t_{12} & s\varepsilon_1 + t_{12} & 2st_{12} \\ \dots & \varepsilon_1 + \varepsilon_2 + V_{12} & 2st_{12} & s\varepsilon_2 + t_{12} \\ \dots & \dots & \varepsilon_1 + \varepsilon_2 + V_{12} & s\varepsilon_2 + t_{12} \\ \dots & \dots & \dots & 2\varepsilon_2 + U_2 \end{pmatrix}$$

but thus renormalized parameters might deviate strongly from initial integrals

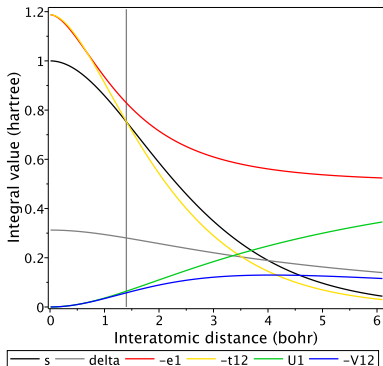
Matrix elements: bare vs parameterized



The experimental equilibrium distance is indicated

Primitive integrals. Not shown:

$$\varepsilon_1^{00} = -1/2, U_1^0 = 5/8$$



The experimental equilibrium distance is indicated

Elements of many-body Hamiltonian in ZDO form

MO basis is good for symmetric systems

In MO basis

$$(|20\rangle \quad |\alpha\beta\rangle \quad |\beta\alpha\rangle \quad |02\rangle)$$

Hamiltonian matrix is sparse with HF SCF energies on its diagonal

$$H = \begin{pmatrix} E_0 + \Delta Y - 2|t| & 0 & 0 & Y \\ \dots & E_0 - \Delta Y & Y & 0 \\ \dots & \dots & E_0 - \Delta Y & 0 \\ \dots & \dots & \dots & E_0 + \Delta Y + 2|t| \end{pmatrix}$$

but basis functions are complex combinations of site orbitals

2c2e model: orthogonalized symmetrized basis

(spin operator can be diagonalized by spin symmetry)

$$\Phi_1 = 20 - 02 = \frac{1}{\sqrt{2(1-s^2)}} (|1_1\rangle - |2_2\rangle)$$

$$\Phi_2 = 20 + 02 = \frac{1}{\sqrt{2(1-s^2)}} (|1_1\rangle + |2_2\rangle) - \frac{s}{\sqrt{2(1-s^2)}} (|1_2\rangle + |2_1\rangle)$$

$$\Phi_3 = \alpha\beta + \beta\alpha = \frac{1}{\sqrt{2(1-s^2)}} (|1_2\rangle + |2_1\rangle) - \frac{s}{\sqrt{2(1-s^2)}} (|1_1\rangle + |2_2\rangle)$$

$$\Phi_4 = \alpha\beta - \beta\alpha = \frac{1}{\sqrt{2(1-s^2)}} (|1_2\rangle - |2_1\rangle)$$

or in coordinate representation

$$\frac{1}{\sqrt{2}} (|1_1\rangle \pm |2_2\rangle) = \frac{\varphi_1(x_1)\varphi_1(x_2) \pm \varphi_2(x_1)\varphi_2(x_2)}{\sqrt{2}} \frac{\chi_\uparrow(\sigma_1)\chi_\downarrow(\sigma_2) - \chi_\downarrow(\sigma_1)\chi_\uparrow(\sigma_2)}{\sqrt{2}}$$

$$\frac{1}{\sqrt{2}} (|1_2\rangle \pm |2_1\rangle) = \frac{\varphi_1(x_1)\varphi_2(x_2) \pm \varphi_2(x_1)\varphi_1(x_2)}{\sqrt{2}} \frac{\chi_\uparrow(\sigma_1)\chi_\downarrow(\sigma_2) \mp \chi_\downarrow(\sigma_1)\chi_\uparrow(\sigma_2)}{\sqrt{2}}$$

... continuation

$$H^{\text{ortho}} = E_0 + \begin{pmatrix} Y - \frac{2s^2}{1-s^2} \frac{U+V}{2} & -2\Delta\varepsilon & s\Delta U & 0 \\ -2\Delta\varepsilon & Y & 2t & 0 \\ s\Delta U & 2t & -Y & 0 \\ 0 & 0 & 0 & -Y - \frac{2s^2}{1-s^2} \frac{U+V}{2} \end{pmatrix}$$

where $Y = \frac{U-V}{2}$. Now the triplet ($S = 1$) is separated:

$$\Phi_4 = \frac{1}{\sqrt{2(1-s^2)}} (| \begin{smallmatrix} 1 \\ 2 \end{smallmatrix} \rangle - | \begin{smallmatrix} 2 \\ 1 \end{smallmatrix} \rangle)$$

This is for $S_z = 0$, the component of the triplet with $S_z = +1$ is

$$\frac{1}{\sqrt{1-s^2}} | \begin{smallmatrix} 1 \\ 2 \end{smallmatrix} \rangle = \alpha\alpha = \frac{1}{\sqrt{1-s^2}} \frac{\varphi_1(x_1)\varphi_2(x_2) - \varphi_2(x_1)\varphi_1(x_2)}{\sqrt{2}} \chi_{\uparrow}(\sigma_1)\chi_{\uparrow}(\sigma_2)$$

Concept: Triplet is usually lower than excited singlet

Yes, by writing

$$\Psi = \sin \theta \cos \phi \Phi_1 + \sin \theta \sin \phi \Phi_2 + \cos \theta \Phi_3$$

one can show that energy gap between the triplet and excited singlet has the sign of $U - V$

Let's now consider symmetric case: then the excited singlet is given by odd function with respect to site interchange:

$$\Phi_1 = \frac{1}{\sqrt{2(1-s^2)}} (|1\rangle - |2\rangle)$$

and the triplet – excited-singlet gap is $U - V$

Three concepts about ee-correlations – #1

Singlet-triplet gap is a measure of correlations

Let's introduce correlation factor:

$$\frac{1 - \langle \Psi^{\text{RHF}} | \Psi^{\text{exact}} \rangle^2}{\langle \Psi^{\text{RHF}} | \Psi^{\text{exact}} \rangle^2} = \tanh^2 \eta$$

In terms of UV parameters

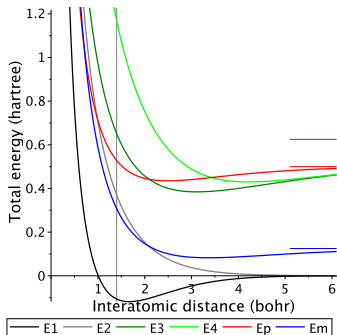
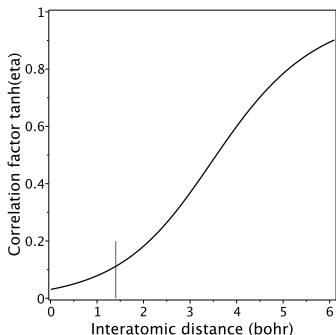
$$\sinh 2\eta = \frac{U - V}{4|t|}$$

Now

$$\frac{E_3 - E_2}{E_3 - E_1} = \frac{U - V}{\frac{U - V}{1 - e^{-4\eta}} - \frac{s^2(U + V)}{1 - s^2}} \approx 1 - e^{-4\eta} \text{ for small } s$$

Three concepts about ee-correlations – #2

At bonding & smaller distances correlations are small, at larger distances correlations grow



The experimental equilibrium distance is indicated

And vice versa: the larger the correlations the smaller the bond strength $E_{\text{bond}} = -2|t|e^{-2\eta}$

The lowest and the highest states have

$$\Psi \sim e^{\mp\eta} (|1\rangle + |2\rangle) \pm e^{\pm\eta} (|\frac{1}{2}\rangle + |\frac{2}{1}\rangle)$$

if correlation factor $\eta = 0$ we get single Slater determinants

Three concepts about ee-correlations – #3

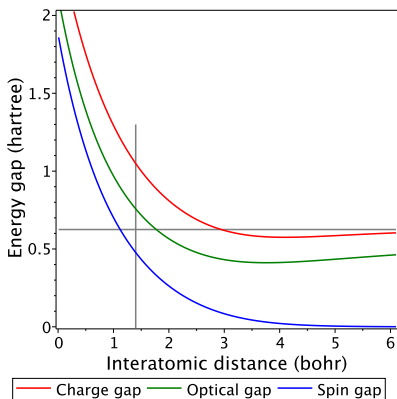
Natural orbital occupations is a measure of correlations

The one-electron density matrix of the ground state is given by

$$\rho^\sigma = \frac{1}{2} \begin{pmatrix} 1 & \cosh^{-1} 2\eta \\ \dots & 1 \end{pmatrix}$$

The eigenvalue of this matrix corresponding to unoccupied MOs is $\frac{\sinh^2 \eta}{\cosh 2\eta}$ and thus indeed is another measure of correlations

Ordering of spin, optical and charge gaps

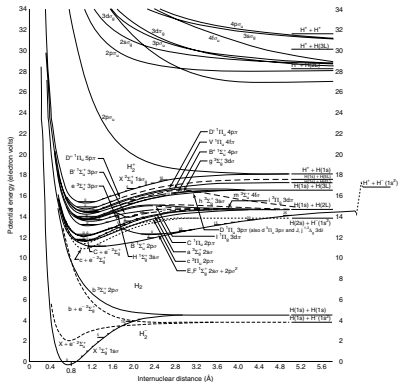
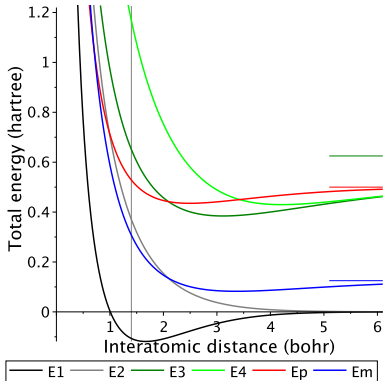


- Spin $E_2 - E_1 = 2|t|e^{-2\eta} - 2\Delta Y$
- Optical $E_3 - E_1 = 2|t|e^{+2\eta} - 2\Delta Y$
- Charge IP - EA = $2|t| (e^{+2\eta} - 1 + e^{-2\eta}) + \frac{V_{12}^0 - X_{12}}{1-s^2} - 2\Delta Y$

If $U > V > 0$ which is natural condition for chemical elements
then spin gap < optical gap < charge gap

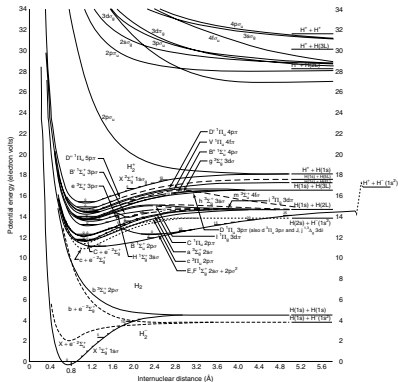
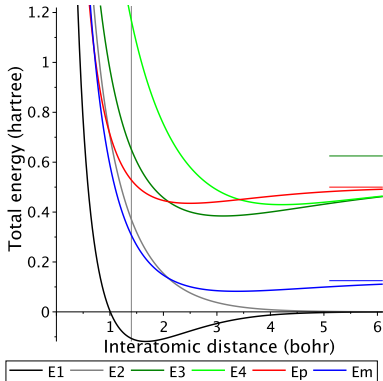
H₂ molecule: model vs real molecule

Orbital relaxations are always important for quantitative accuracy



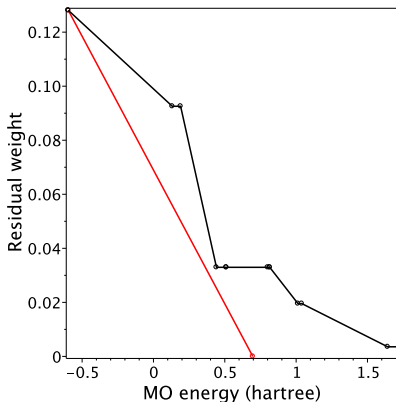
H₂ molecule: model vs real molecule

Orbital relaxations are always important for quantitative accuracy



Another view on orbital relaxations

AO constituting HOMO produces upshifted LUMO, whereas real LUMO has little contribution from that AO



Residual weight of HOMO AO in other MOs calculated as $1 - \sum_{\text{MO}:\epsilon(\text{MO}) < \epsilon} \langle \psi_{\text{MO}} | \psi_{\text{AO}} \rangle^2$: Def2-QZVP vs. one-orbital approximation

Concept: Tight binding is accurate at bonding distances

If we fit exact many-body Hamiltonian

$$H = \begin{pmatrix} 2\varepsilon_1 + U_1 & s\varepsilon_1 + t_{12} & s\varepsilon_1 + t_{12} & 2st_{12} \\ \dots & \varepsilon_1 + \varepsilon_2 + V_{12} & 2st_{12} & s\varepsilon_2 + t_{12} \\ \dots & \dots & \varepsilon_1 + \varepsilon_2 + V_{12} & s\varepsilon_2 + t_{12} \\ \dots & \dots & \dots & 2\varepsilon_2 + U_2 \end{pmatrix}$$

by tight binding model (nonorthogonal, but s is not fitted)

$$H^{\text{TB}} = \begin{pmatrix} 2\tilde{\varepsilon}_1 & s\tilde{\varepsilon}_1 + \tilde{t} & s\tilde{\varepsilon}_1 + \tilde{t} & 2s\tilde{t} \\ \dots & \tilde{\varepsilon}_1 + \tilde{\varepsilon}_2 & 2s\tilde{t} & s\tilde{\varepsilon}_2 + \tilde{t} \\ \dots & \dots & \tilde{\varepsilon}_1 + \tilde{\varepsilon}_2 & s\tilde{\varepsilon}_2 + \tilde{t} \\ \dots & \dots & \dots & 2\tilde{\varepsilon}_2 \end{pmatrix}$$

then for the hydrogen molecule the relative error of the diagonal elements is less than **4%**; for the nondiagonal elements the error is negligible, less than **0.1%**

Of course, we cannot fit different charge states by the same parameters

2c2e model beyond single bond: correlations in acenes

Diradical or strongly correlated?

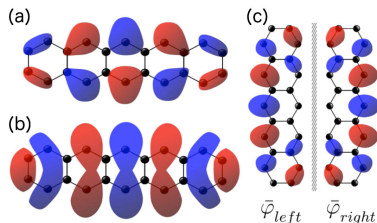


FIG. 1. (a) HOMO isosurface of the pentacene molecule as obtained by LDA calculations in a Gaussian basis set. b) As in panel (a), but for the LUMO. (c) Edge orbitals in pentacene obtained as symmetric and antisymmetric linear combinations of HOMO and LUMO.

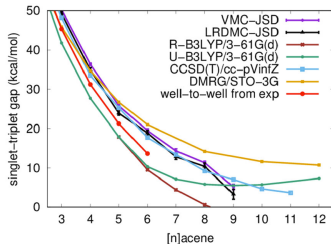


FIG. 2. Adiabatic (“well-to-well”) singlet-triplet gap as a function of the number of rings in the molecule, for different theories: variational and diffusion Monte Carlo with JSD wave function (VMC-JSD and LRDMC-JSD, this work), restricted and unrestricted B3LYP (R-B3LYP and U-B3LYP, Ref. 30), CCSD(T) with focal point analysis,^{10,34} DMRG/CASCI in STO-3G minimal basis set (DMRG, Ref. 9), the experimental gap where the zero point energy (ZPE) contribution has been subtracted (ZPE and experimental values from Ref. 34).

N Dupuy, M Casula, Fate of the open-shell singlet ground state in the experimentally accessible acenes: A quantum Monte Carlo study, J Chem Phys 148, 134112 (2018)

Questions

1. Give physical interpretation for two basis functions constituting ground state

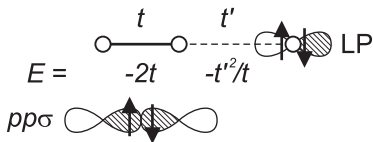
$$\Psi \sim e^{-\eta} (|1\rangle_1 + |2\rangle_2) + e^{\eta} (|1\rangle_2 + |2\rangle_1)$$

2. What atomic orbitals would you add to improve the accuracy for the hydrogen molecule?
3. Usually a bond is broken when being elongated. Give example of “bond breaking” without changing distance between the two atoms.

3c4e model of hypervalent and secondary bonding

Let's consider only molecular orbital theory

$$H = \begin{pmatrix} 0 & t & 0 \\ t & 0 & t' \\ 0 & t' & 0 \end{pmatrix}$$



- There are three MOs: bonding, nonbonding and antibonding
- The total MO energy $E = -2\sqrt{t^2 + t'^2} \approx -2t - t'^2/t$ consists of covalent and **secondary bond** energies

- Bond orders

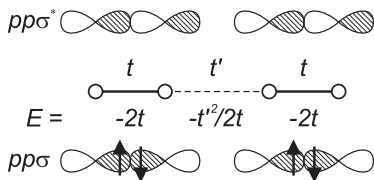
$$B_{12} = \frac{t^2}{t^2 + t'^2}, \quad B_{23} = \frac{t'^2}{t^2 + t'^2}$$

illustrate **trans-influence rule**: the stronger the secondary bond the weaker the covalent one

- In the limit $t' = t$ we have 3c4e **hypervalent bonding**: it is stronger than single covalent bond by factor of $\sqrt{2}$, but weaker than two single bonds by the same factor

4c4e dimer model: dispersion force

$$H^{1e} = \begin{pmatrix} 0 & t & 0 & 0 \\ t & 0 & t' & 0 \\ 0 & t' & 0 & t \\ 0 & 0 & t & 0 \end{pmatrix}$$



In the 2nd-order perturbation theory the two dimers attract by secondary bonding and **dispersion force** (polarization):

$$-\frac{e^{-6\eta}}{\cosh^2 2\eta} \frac{\Delta V^2}{8E_{\text{gap}}}, \quad \Delta V = V_{13} - V_{14} - V_{23} + V_{24}, \quad E_{\text{gap}} = 2|t|$$

because if V is Coulomb potential then at large intermolecular separations

$$\Delta V^2 = \frac{[3(\mathbf{nd}_1)(\mathbf{nd}_2) - (\mathbf{d}_1\mathbf{d}_2)]^2}{r^6}$$

4c4e dimer model: solvatochromism

$$H^{1e} = \begin{pmatrix} -V_1 - V_{13} - V_{14} & t_1 & 0 & 0 \\ t_1 & -V_1 - V_{23} - V_{24} & 0 & 0 \\ 0 & 0 & -V_2 - V_{13} - V_{23} & t_2 \\ 0 & 0 & t_2 & -V_2 - V_{14} - V_{24} \end{pmatrix}$$

The 2nd order correction to the transition energy to the first excited singlet of the 1st dimer is given by

$$\Delta E_{13}^{(2)} = \frac{\Delta V^2 e^{-2\eta_1 - 2\eta_2}}{8 \cosh 2\eta_1 \cosh 2\eta_2} \left(\frac{1}{|t_1|e^{2\eta_1} - |t_2|e^{2\eta_2}} + \frac{1}{|t_1|e^{2\eta_1} + |t_2|e^{2\eta_2}} - \frac{e^{4\eta_1}}{|t_2|e^{2\eta_2} + |t_1|e^{-2\eta_1}} \right)$$

- The three terms correspond to different virtual transitions in 1st dimer while 2nd dimer is in the virtually excited singlet: $3 \rightarrow 1$, $1 \rightarrow 3$ (correction to the ground state), $3 \rightarrow 4$
- The changes in the transition energy (**solvatochromism**) is of the same nature as the dispersion force
- The sign depends on parameters: if studied excitation is the lowest excitation in the entire system then we have redshift

4c4e dimer model: energy transfer

$$H^{1e} = \begin{pmatrix} -V - V_{13} - V_{14} & t & 0 & 0 \\ t & -V - V_{23} - V_{24} & 0 & 0 \\ 0 & 0 & -V - V_{13} - V_{23} & t \\ 0 & 0 & t & -V - V_{14} - V_{24} \end{pmatrix}$$

We have resonance

- At the first order the excited state is split into a pair of levels (**Forster transfer**):

$$E_{13} \approx 2|t|e^{2\eta} \pm \frac{\Delta V}{e^{4\eta} + 1}$$

- Note that t' does not enter this formula, so that the **Dexter transfer** is of the “second order”
- For triplets the first order correction is zero even at resonance

Onsite 2c2e model: Hund's rule (model of O₂ molecule)

$$H = \begin{pmatrix} U & 0 & 0 & X \\ \dots & V & X & 0 \\ \dots & \dots & V & 0 \\ \dots & \dots & \dots & U \end{pmatrix}$$

Because $U > V > 0$ and $X > 0$

- The lowest state is the triplet Φ_4 (or $\alpha\alpha$) with energy $V - X$
- The next two levels are singlets Φ_1 (or $20 - 02$) and Φ_3 (or $\alpha\beta + \beta\alpha$) with energies $U - X$ and $V + X$ respectively
- The highest state is Φ_2 (or $20 + 02$) with energy $U + X$.

Onsite 2c2e model: orbital relaxation in O₂ molecule

- If there is a rotational symmetry then $U - V = 2X$ and thus $\Phi_{1,3}$ are degenerate
- In fact, orbital relaxation occurs breaking the symmetry and lowering the single-determinant state $|\frac{1}{1}\rangle$ (or 20)
- O₂ example:
 - ▶ ground state is triplet ${}^3\Sigma_g^-$
 - ▶ the lowest singlet is the symmetry-broken ${}^1\Delta_g$ at 0.98 eV
 - ▶ it is followed by symmetric singlet ${}^1\Sigma_g^+$ separated by 0.65 eV
 - ▶ The estimated exchange integral $X = 0.5$ eV and the orbital relaxation energy is 0.65 eV per two electrons

Onsite 3c3e model: atomic levels (and orbital relaxation)

NIST data for P

In the rotationally symmetric case there are 3 levels:

- the ground state is the quartet 4S with energy $-3X$
- the first excited state is 2D at zero energy
- it is followed by 2P state at $2X$

If the condition $U - V = 2X$ is broken, then the energy of the state 2P is $U - V$, whereas the state 2D splits into doubly degenerate state at zero energy and triply degenerate state at $U - V - 2X$. In fact, 2D symmetry is exact, whereas other deviations are signatures of orbital relaxation. Here are NIST data:

- for nitrogen the estimated value of X is 0.79 eV by $^4S-^2D$ transition and 0.60 eV by $^2D-^2P$ transition
- phosphorus 0.47 vs 0.46 eV
- arsenic 0.44 vs 0.48 eV

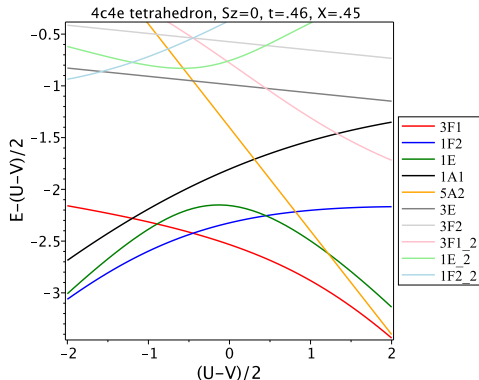
4c4e tetrahedral model: strong static correlations

- In 1e picture there are doubly occupied a_1 MO and two electrons on triply degenerate t_2 MO
- Thus the ground state is 9-fold degenerate: 6 singlets $[F_2 \times F_2] = {}^1A_1 + {}^1E + {}^1F_2$ and 3 triplets $\{F_2 \times F_2\} = {}^3F_1$
- Only the quartet 5A_2 state is nondegenerate

In fact ee-interaction removes the degeneracy by creating charge and spin density waves

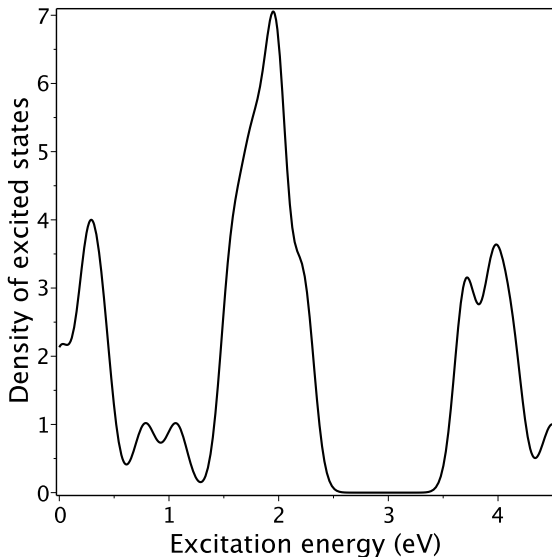
4c4e tetrahedral model: degeneracy has been lowered

- Orthogonalized AOs
- $H_{ij}^{1e} = \delta_{ij} - 1 - 3V\delta_{ij}$
- U, V, X, u, v, x, w
- e-h symmetry
 $Y = (U - V)/2$



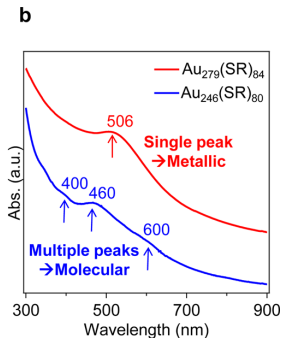
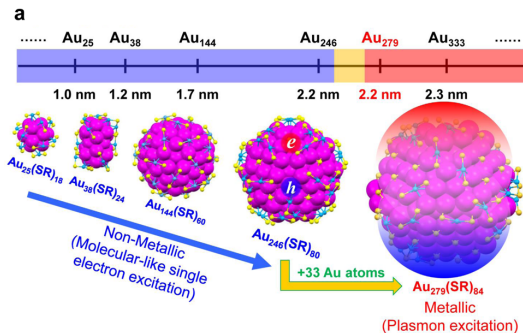
- The essential physics of this model can be understood in terms of only two parameters: X and Y
- $X = 0.45$ and $Y = 0.09$ if parameterized by Li_4 cluster FCI/cc-pVQZ calculations of the 5 lowest states
- The lowest 3F_1 and 1F_2 correspond to bond-order wave (BOW) with D_{2d} (antiprism) pattern
- The remaining degeneracy is removed by deformations

4c4e tetrahedral model: it is still “metal-like”



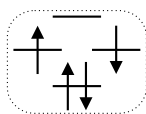
Boundary between bulk metal and atomic cluster

R Jin, T Higaki, Commun Chem 4, 28 (2021)

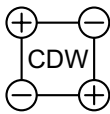


4c4e ring model: density waves

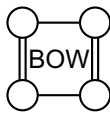
$$H^{1e} = \begin{pmatrix} 0 & t & 0 & t \\ t & 0 & t & 0 \\ 0 & t & 0 & t \\ t & 0 & t & 0 \end{pmatrix}$$



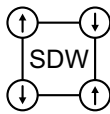
MOs for
 $U=V=0$



large V
2 states

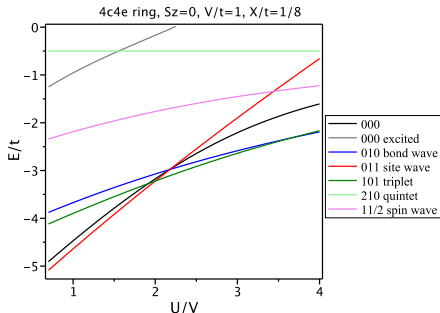


$U=2V$
4 states



large U
6 states

- Ground state degeneracy
- Three kinds of electron density waves
- Levels crowding at large U
- Two Slater determinants for variational function

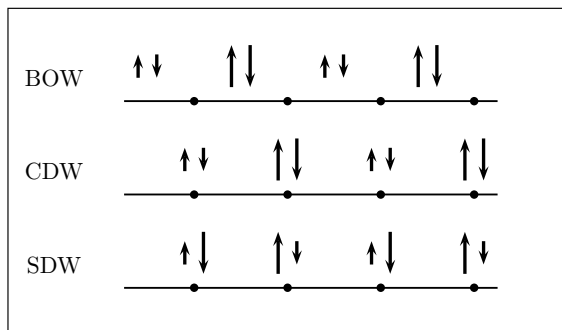


BOW=bond order wave, CDW=charge density wave, SDW=spin density wave

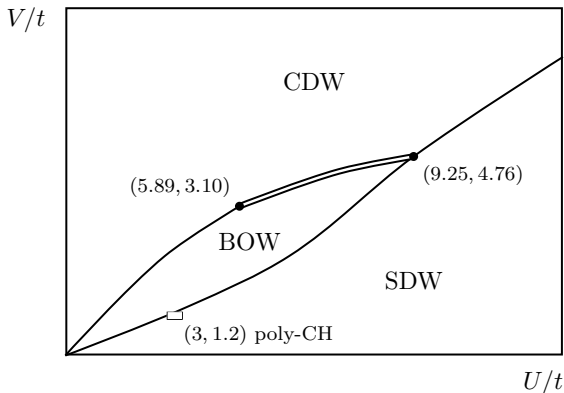
1D extended Hubbard model

$$H = \epsilon \sum_{i \in \mathbb{Z}} (-1)^i n_i + \sum_{i \in \mathbb{Z}} (t + (-1)^i \delta t) T_{i,i+1} + U \sum_{i \in \mathbb{Z}} n_i^\uparrow n_i^\downarrow + V \sum_{i \in \mathbb{Z}} n_i n_{i+1}$$

Standard model: $\epsilon = 0$ and $\delta t = 0$. Nonzero ϵ stabilizes CDW, nonzero δt stabilizes BOW



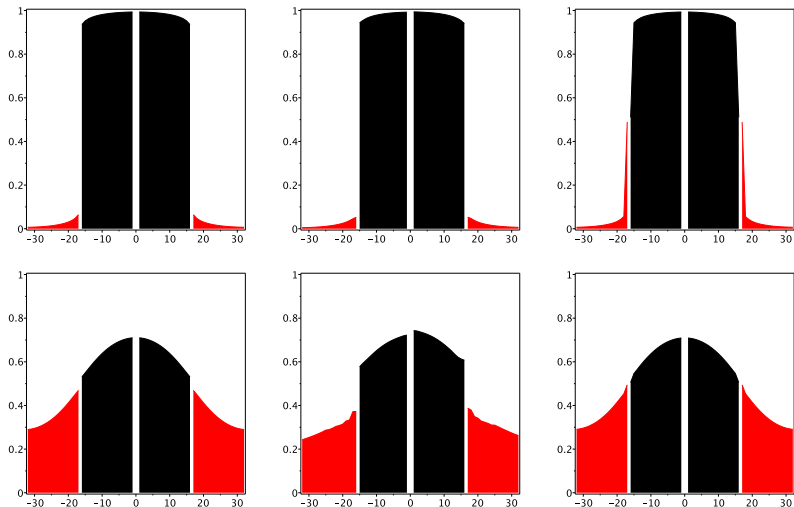
1D extended Hubbard model at half filling



Phase diagram (in fact the width of BOW phase is only tenths of t). Double line means the first order transition, single line – continuous transition. Coordinates of the tricritical point (left) and critical end point (right) are from [PRL 99, 216403 (2007)]

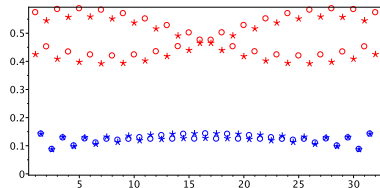
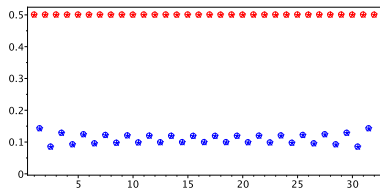
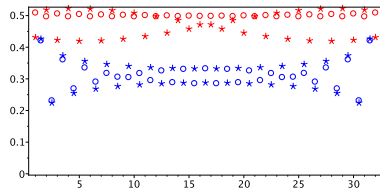
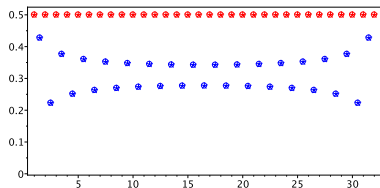
1D extended Hubbard model: population analysis

ground state, hole, exciton; $U/V = 2/1$ vs $16/4$; $L=32$ open, DMRG 4 swipes 500 states



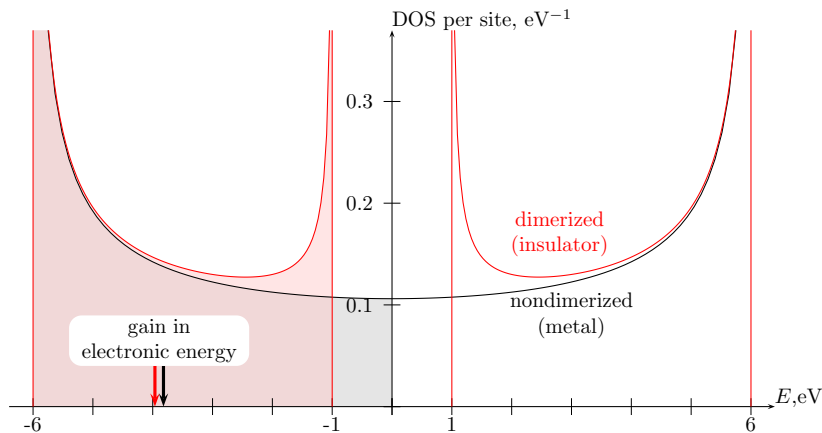
1D extended Hubbard model: density waves

1e density matrix (diagonal & subdiagonal): ground state & hole; $U/V = 2/1$ vs $16/4$

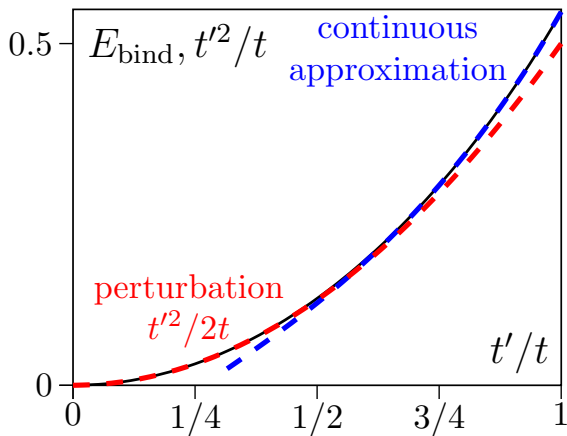


1D Peierls model or Su-Schrieffer-Heeger model

$$H = \sum_{i \in \mathbb{Z}} t(u_i) T_{i,i+1} + \frac{1}{2M} \sum_{i \in \mathbb{Z}} p_i^2 + \frac{K}{2} \sum_{i \in \mathbb{Z}} u_i^2$$



Peierls transition vs Jahn–Teller effect



Take-home message

Many if not most complex phenomena in quantum chemistry and condensed matter theory can be conceptually understood on basis of small-size models