

Many Electron Theory:

Particles and holes. Unitary transformations.

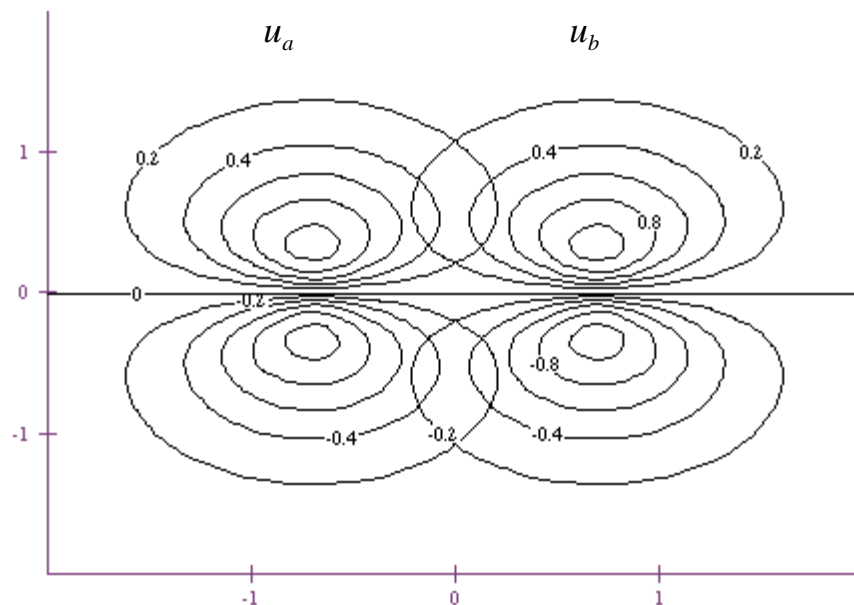
Continued notes for a workgroup September-October 2002.

Equivalencies in the Pariser-Parr-Pople model.

Hückel established a remarkably useful model for the characterization of conjugated systems, particularly the catacondensed aromatic hydrocarbons. Charles Coulson and his students, especially H. C. Longuet-Higgins gave this model a rather unique status as both a tool for the applied chemist and a formalism that served to develop concepts such as charges and bond orders. The one-electron picture in the Hückel model cannot account for spectra such that triplets and singlets are different. Thus it came to Pariser and Parr and to Pople to offer the generalization which carries their name.

Basic to the PPP-model is the appreciation of the smallness of Coulomb interaction integrals that involve products of atomic orbitals that are orthogonal. The spin orbital basis, $B: \{u_s | s = 1, 2, \dots, M\}$, is now the set of so called π -orbitals, two of opposite spin for each atom. We extend the notation so that the basis is $B: \{u_s, u_{-s} | s = 1, 2, \dots, M\}$. Negative subscripts refer to β -type spin orbitals, while positive ones concern α -type. Standard atomic orbitals are nonorthogonal with overlap integrals between neighboring atoms in the range 0.2-0.3. Löwdin orthogonalization offers an orthonormal set, *as similar as possible to the original one*.

An illustration from the ethylene molecule serves as an indicator for the reasons behind the concept of *Zero Differential Overlap, ZDO*. Two simple Slater type atomic orbitals $u_a(\mathbf{r}), u_b(\mathbf{r})$ are centered on the two carbon nuclei and give contour diagrams in a plane through the nuclei perpendicular to the molecular plane such as in Fig. 1:

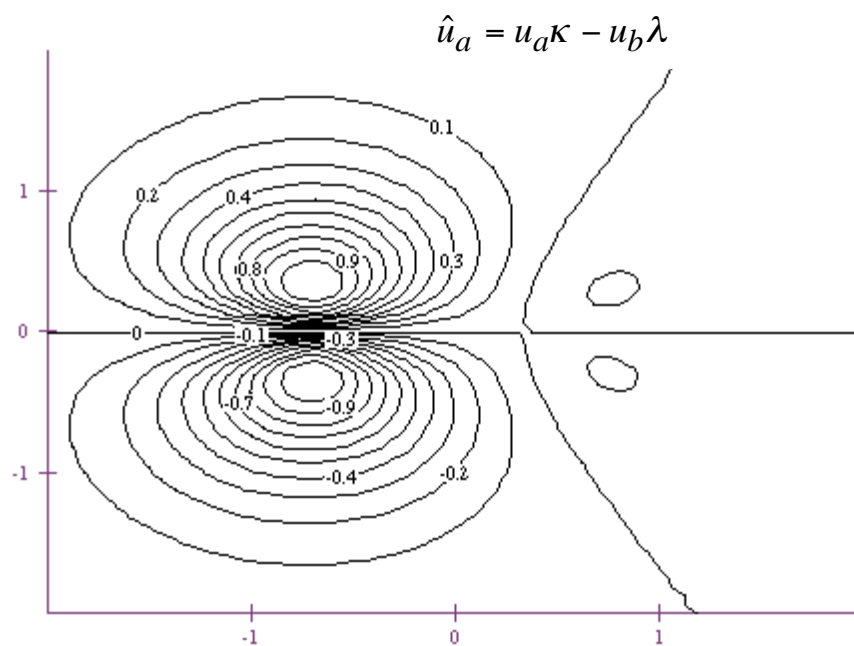


Their overlap integral is S , the symmetrically orthonormalized orbitals are

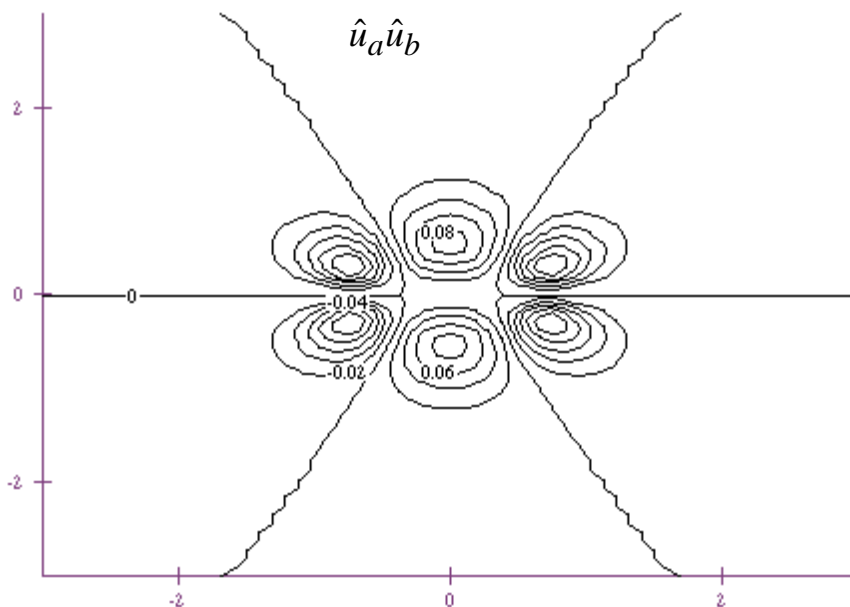
$$\hat{u}_a = u_a\kappa - u_b\lambda; \hat{u}_b = u_b\kappa - u_a\lambda;$$

$$\kappa = \frac{\cos(\omega)}{\cos(2\omega)}; \lambda = \frac{\sin(\omega)}{\cos(2\omega)}; \sin(2\omega) = S.$$

They have diagrams such as in Fig. 2:



A slight distortion is present. The product density of the orthonormal orbitals gives a density as given in Fig. 3:



Regions of positive and negative density alternate and have small amplitudes. Calculations have shown that Coulomb integrals involving this density give small values. Neglect of such integrals constitutes *ZDO*.

Hückel neglected matrix elements between orbitals that are farther away than neighboring atoms. This feature is normally used in the PPP model as well. The model hamiltonian is then

$$\begin{aligned}
 H(PPP) = & \sum_r \alpha_r (a_r^\dagger a_r + a_{-r}^\dagger a_{-r}) + \sum_{rs} \beta_{rs} (a_r^\dagger a_s + a_{-r}^\dagger a_{-s}) \\
 & + \sum_r \gamma_{rr} a_r^\dagger a_r a_{-r}^\dagger a_{-r} + \frac{1}{2} \sum_{r \neq s} \gamma_{rs} (a_r^\dagger a_r + a_{-r}^\dagger a_{-r}) (a_s^\dagger a_s + a_{-s}^\dagger a_{-s}) \\
 (pq | rs) = & \delta_{pq} \delta_{rs} \gamma_{pr}
 \end{aligned}$$

Alternant hydrocarbons are those where the carbon atoms can be separated into two disjoint subsets so that an atom in one set only has neighbors in the other set. Numbering can then be arranged so that one set is labeled by

even numbers, or *starred* as used conventionally, and the other then has odd labels and are *unstarred*. Matrix elements β_{rs} equal zero when both indices are either even or odd.

It was shown in Hückel theory that there is a pairing between occupied and unoccupied molecular orbitals for alternant hydrocarbons and it was later demonstrated that the PPP model preserves this feature. It is a consequence of a symmetry operation that is represented by a unitary operator. Here we consider the form

$$U = \exp(\Pi); \Pi = \frac{\pi}{2} \sum_r (-)^r (a_r^\dagger a_{-r}^\dagger - a_{-r} a_r) = -\Pi^\dagger$$

The elementary annihilation and creation operators transform as follows

$$\begin{aligned} [a_r, \Pi] &= \frac{\pi}{2} (-)^r [a_r, a_r^\dagger a_{-r}^\dagger] = \frac{\pi}{2} (-)^r a_{-r}^\dagger; \\ [a_{-r}, \Pi] &= \frac{\pi}{2} (-)^r [a_{-r}, a_r^\dagger a_{-r}^\dagger] = -\frac{\pi}{2} (-)^r a_r^\dagger; \\ [a_r^\dagger, \Pi] &= -\frac{\pi}{2} (-)^r [a_r^\dagger, a_{-r} a_r] = \frac{\pi}{2} (-)^r a_{-r}; \\ [a_{-r}^\dagger, \Pi] &= -\frac{\pi}{2} (-)^r [a_{-r}^\dagger, a_{-r} a_r] = -\frac{\pi}{2} (-)^r a_r; \end{aligned}$$

and thus

$$\begin{aligned} U a_r^\dagger U^\dagger &= -(-)^r a_{-r}; U a_{-r}^\dagger U^\dagger = (-)^r a_r; \\ U a_r U^\dagger &= -(-)^r a_{-r}^\dagger; U a_{-r} U^\dagger = (-)^r a_r^\dagger; \end{aligned}$$

The transformation of the hamiltonian can then be worked out to be

$$\begin{aligned} UH(PPP)U^\dagger &= \sum_r \alpha_r (a_{-r} a_{-r}^\dagger + a_r a_r^\dagger) + \sum_{rs} \beta_{rs} (-)^{r-s} (a_{-r} a_{-s}^\dagger + a_r a_s^\dagger) \\ &+ \sum_r \gamma_{rr} a_{-r} a_{-r}^\dagger a_r a_r^\dagger + \frac{1}{2} \sum_{r \neq s} \gamma_{rs} (a_{-r} a_{-r}^\dagger + a_r a_r^\dagger) (a_{-s} a_{-s}^\dagger + a_s a_s^\dagger) \\ &= \sum_r (2\alpha_r + \gamma_{rr} + 2 \sum_s \gamma_{rs}) (1 - a_r^\dagger a_r - a_{-r}^\dagger a_{-r}) + H(PPP) \end{aligned}$$

and with certain conditions there is an invariance under this transformation.

The dipole moment operator is represented, in the PPP model, as

$$\mathbf{D} = \sum_r e \mathbf{R}_r (a_r^\dagger a_r + a_{-r}^\dagger a_{-r})$$

and is "odd" under the transformation. So is the dipole velocity operator,

$$\dot{\mathbf{D}} = \frac{1}{i\hbar} [\mathbf{D}, H(PPP)] = \frac{e}{i\hbar} \sum_{rs} (\mathbf{R}_r - \mathbf{R}_s) \beta_{rs} (a_r^\dagger a_s + a_{-r}^\dagger a_{-s})$$

The determination of optical rotatory power requires a representation of the magnetic moment operator. London considered the diamagnetic properties of conjugated systems in the Hückel model and concluded that a proper form for the introduction of a magnetic field in the hamiltonian was to let the orbitals be field dependent and to obtain field dependent β -parameters:

$$\beta_{rs}(\mathbf{B}) = \beta_{rs}(0) \exp\left[-\frac{ie}{2\hbar c} \mathbf{B} \cdot (\mathbf{R}_r \wedge \mathbf{R}_s)\right]$$

It follows that

$$\begin{aligned} H(PPP; \mathbf{B}) &= H(PPP; 0) - \mathbf{B} \cdot \mathbf{M} + \dots \\ &= H(PPP; 0) - \mathbf{B} \cdot \sum_{rs} \frac{ie}{2\hbar c} (\mathbf{R}_r \wedge \mathbf{R}_s) \beta_{rs} (a_r^\dagger a_s + a_{-r}^\dagger a_{-s}) + \dots \end{aligned}$$

and the result is that the magnetic moment operator changes sign under the transformation.

NOTES: J. L. & Y. Ö.: Derivation and Analysis of the Pariser-Parr-Pople Model *J. Chem. Phys.* **49**(1968)716.

J. L. Consistency Requirement in the Pariser-Parr-Pople Model. *Chem. Phys. Lett.* **1**(1967)39.

J. Michl: Several papers in JACS on magneto-optical properties in 1976-8(?)

J. L. & J. Michl:

On the Inherent Optical Activity of Organic Disulfides *J. Am. Chem. Soc.* **92**(1970)2619.

Perturbation expansion, van Vleck forms.

Conflicting views on the bonding in conjugated systems, the valence bond or resonance theory as opposed to molecular orbital descriptions, are illuminated by a study of the PPP-model in the limit of separated atoms. This is the situation when the β -parameters are considered small and the term where they occur in the hamiltonian is taken as a perturbation. The other terms commute with the atomic number operators, $n_r = a_r^\dagger a_r + a_{-r}^\dagger a_{-r}$, and zeroth order states are determined only by the eigenvalues of these. Normally we expect that all atoms have one electron and there will then be a manifold of 2^M degenerate states to be dealt with by degenerate perturbation theory. Van Vleck considered such a problem by means of unitary transformations.

A general operator approach to perturbation theory considers the form

$$\begin{aligned} & \exp(i\Theta)[H + V]\exp(-i\Theta) \\ &= H + \{V + i[\Theta, H]\} + \left\{i[\Theta, V] - \frac{1}{2}[\Theta, [\Theta, H]]\right\} + \dots \end{aligned}$$

and the idea is to eliminate the first order term,

$$V + i[\Theta, H] = 0$$

so that

$$\exp(i\Theta)[H + V]\exp(-i\Theta) = H + \frac{i}{2}[\Theta, V] + \dots$$

The analysis is limited here to first order terms in Θ .

A solution to the first order equation is obtained by observing that

$$\frac{d}{dt} \left[e^{iHt} \Theta e^{-iHt} \right] = ie^{iHt} [H, \Theta] e^{-iHt} = -e^{iHt} V e^{-iHt}$$

and that

$$\begin{aligned}
e^{iHt} a_r^\dagger e^{-iHt} &= a_r^\dagger \exp\left(it\alpha_r + it\gamma_{rr} a_{-r}^\dagger a_{-r} + it \sum_{s \neq r} \gamma_{rs} n_s\right) \\
&= a_r^\dagger a_{-r} a_{-r}^\dagger \exp\left(it\alpha_r + it \sum_{s \neq r} \gamma_{rs} n_s\right) \\
&\quad + a_r^\dagger a_{-r}^\dagger a_{-r} \exp\left(it\alpha_r + it\gamma_{rr} + it \sum_{s \neq r} \gamma_{rs} n_s\right)
\end{aligned}$$

The exponential operators commute with the others. Further algebraic manipulations leads to an expression for the second order perturbation operator that is expressed in terms of atomic spin operators:

$$\mathbf{S}_r = \frac{\mathbf{e}_x}{2} (a_r^\dagger a_{-r} + a_{-r}^\dagger a_r) + \frac{i\mathbf{e}_y}{2} (-a_r^\dagger a_{-r} + a_{-r}^\dagger a_r) + \frac{\mathbf{e}_z}{2} (a_r^\dagger a_r - a_{-r}^\dagger a_{-r})$$

The result is a Heisenberg spin hamiltonian of the form

$$\begin{aligned}
H_{eff} &= -\sum_{rs} J_{rs} \left(\frac{1}{2} + \mathbf{S}_r \cdot \mathbf{S}_s\right) \\
J_{rs} &= -\frac{\beta_{rs}\beta_{sr}}{\Delta_{rs}} - \frac{\beta_{sr}\beta_{rs}}{\Delta_{sr}} \approx -\frac{2\beta^2}{\Delta} \\
\Delta_{rs} &= \alpha_r - \alpha_s + \gamma_{rr} - \gamma_{rs} + \sum_{p \neq r,s} (\gamma_{rp} - \gamma_{sp}) \langle n_p \rangle
\end{aligned}$$

This hamiltonian acts in the space where there is precisely one electron on every atomic site.

Negative values for the effective exchange integrals J indicates a preference for antiparallel arrangements of spins on neighboring atoms and a possible pairing of orbitals into spin singlets, the valence bond type functions. Eigenstates of the effective hamiltonian can be worked out from the rules of valence bond theory as given by Eyring-Walter-Kimball.

Josef Paldus has studied the PPP-model extensively and with regard to perturbation theory and Al Matsen has given an extensive account of the use of the symmetric group for hamiltonians such as the PPP one. The Hubbard model obtains when only one-center γ 's are kept.