VB THEORY FOR SOLIDS?
(wishful thinking)

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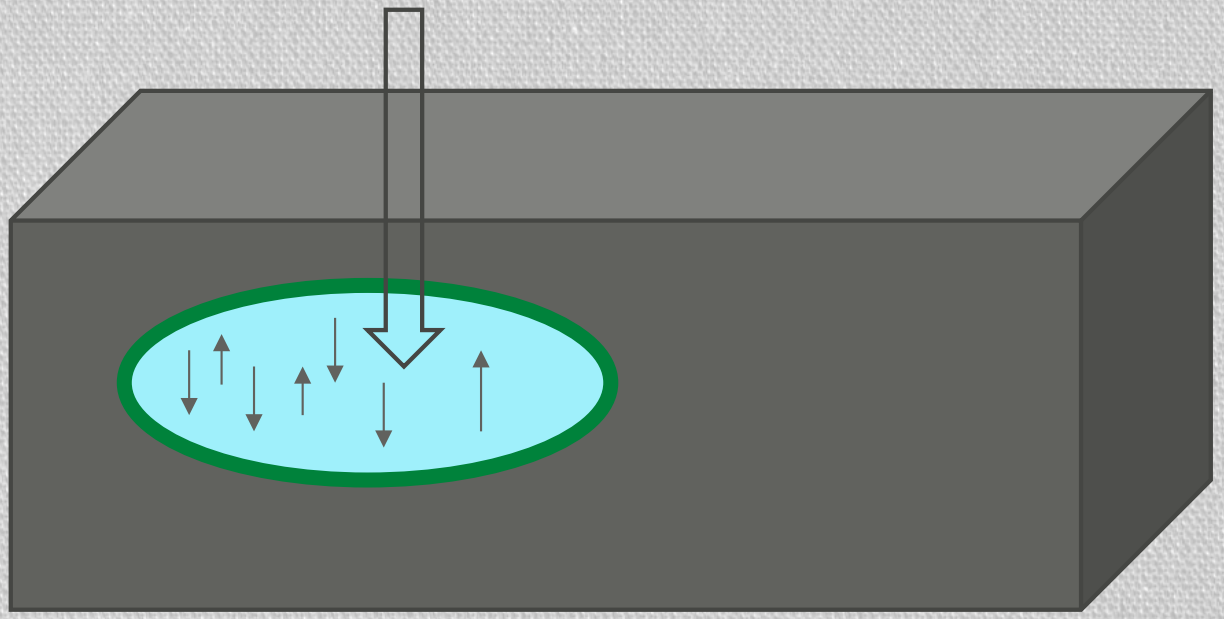
Info on spin manifold?



J. Gerratt

General Theory of Spin-Coupled Wave Functions for Atoms and Molecules

Advances in Atomic and Molecular Physics, Volume 7, 1971, Pages 141-221

Let us consider the following N-electron spin-coupled valence-bond wave function:

$$\Psi_{SM} = \sqrt{N!}\,\hat{A}\{\phi_1(\boldsymbol{r_1})\phi_2(\boldsymbol{r_2})\phi_3(\boldsymbol{r_3})\cdots\phi_N(\boldsymbol{r_N})\Phi_S^N(\sigma_1,\sigma_2,\sigma_3,\ldots,\sigma_N)\} \qquad (1)$$

with

$\{\phi_i\}$ one-electron (singly occupied) orbital,
$\{\boldsymbol{r}_i\}$ spatial electron coordinate
$\{\sigma_i\}$ spin electron coordinate

Symmetric Group
S_N

N-electron spin function:

$$\Phi_S^N = \sum_{k=1}^{f_S^N} C_{Sk}\Theta_{SM;k}^N \qquad (2)$$

with

$$f_S^N = \frac{(2S+1)N!}{\left(\frac{N}{2}+S+1\right)!\left(\frac{N}{2}-S\right)!}. \qquad (3)$$

Point: Is there a way of transforming Eq(2) to a "*reciprocal spin space*"?

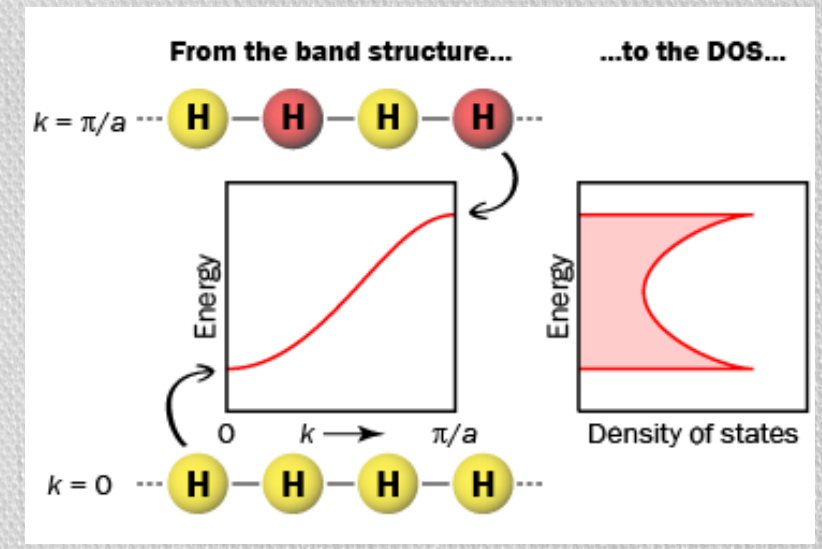
(courtesy by David Cooper)

Fourier-Transform?
Dual space?
Biorthogonal space?

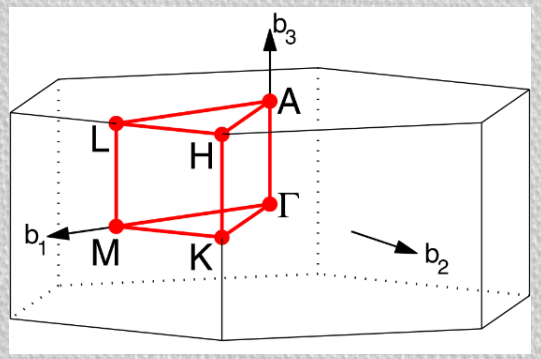
N-electron spin function:

$$\Phi_S^N = \sum_{k=1}^{f_S^N} C_{Sk} \Theta_{SM;k}^N$$

Band structure theory



First Brillouin zone (hcp)



SPIN MANIFOLD/STRUCTURE?
k-points „not constant"?
(embed spin manifold into k?
elsewhere?)

Crystalline orbitals

$$\psi_i(\mathbf{r};\mathbf{k}) = \sum_{\mu} a_{\mu,i}(\mathbf{k})\phi_\mu(\mathbf{r};\mathbf{k})$$

$$\mathbf{F}(\mathbf{k})\mathbf{A}(\mathbf{k}) = \mathbf{S}(\mathbf{k})\mathbf{A}(\mathbf{k})\mathbf{E}(\mathbf{k})$$

Bloch functions

$$\phi_\mu(\mathbf{r};\mathbf{k}) = \sum_{\mathbf{g}} \varphi_\mu(\mathbf{r} - \mathbf{A}_\mu - \mathbf{g})\, e^{i\mathbf{k}\cdot\mathbf{g}}$$

AO

$$\mathbf{F}(\mathbf{k}) = \sum_{\mathbf{g}} \mathbf{F}^{\mathbf{g}}\, e^{i\mathbf{k}\cdot\mathbf{g}}$$

Periodic MP2, RPA, and Boundary Condition Assessment of Hydrogen Ordering in Ice XV

Mauro Del Ben, Joost VandeVondele, and Ben Slater
J. Phys. Chem. Lett., 2014, 5 (23), pp 4122–4128
DOI: 10.1021/jz501985w

- Fully periodic MP2 and RPA approaches

Incrementally Corrected Periodic Local MP2 Calculations: I. The Cohesive Energy of Molecular Crystals

Carsten Müller and Denis Usvyat
J. Chem. Theory Comput., 2013, 9 (12), pp 5590–5598
DOI: 10.1021/ct400797w

- Periodic Hartree–Fock (HF) coupled with the local second order Møller–Plesset perturbation theory (LMP2)

- Towards an exact description of electronic wavefunctions in real solids George H. Booth, Andreas Grüneis1,2, Georg Kresse, Ali Alavi, Nature 493 (2013) 365
- Gaussian-Based Coupled-Cluster Theory for the Ground-State and Band Structure of Solids, James McClain, Qiming Sun, Garnet Kin-Lic Chan, Timothy C. Berkelbach, J. Chem. Theory Comput. 13 (2017) 1209