Tea seminar of “Elektronische Korrelationen”

A Green’s Function Formalism for Ab Initio Band Structure Calculations in Semiconductors and Insulators

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6 July 2003

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1 Introduction

Band structure calculations are dominated by density functional theory (DFT). DFT relies on the ground state electron density. If the exact density functional were known, DFT would be an exact ground state method. In solid state physics the local density approximation (LDA) is the predominantly used functional.

Why is it desirable, despite of the success of DFT, to have alternative approaches to band structures?

- DFT cannot be improved in a well defined way. Especially there are no error estimates for band structures apart from numerical accuracy.

- For example hydrogen bonded systems, like water, are poorly described by DFT. The LDA produces totally wrong results. (LDA is off by more than 200% for cohesive energies in hydrogen fluorine chains)
- DFT yields one-particle bands for the inner valence! Breakdown of the one-particle picture of ionization is not described. (Inner valence is the region in ionization spectra which is energetically well-separated from the outer most IPs. For example the in neon: $1s$: core, $2s$: inner valence, $2p$: core)

In the group of Fulde we pursue a completely different idea. Hartree-Fock is known to be a satisfactory approximation for insulators and semiconductors.

2 Hartree-Fock Approximation

Ab initio electronic structure calculations of crystals in Hartree-Fock approximation employ the non-relativistic *electronic Hamiltonian* (Fixed-nuclei approximation)

$$\hat{H} = \sum_{i=1}^{N_0 N} \hat{h}_i + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N_0 N} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

with the one-electron Hamiltonians

$$\hat{h}_i = -\frac{1}{2}\Delta_i - \sum_{j=1}^{N_0} \sum_{A=1}^{M} \frac{Z_{\vec{R}_j A}}{|\vec{r}_i - \vec{r}_{\vec{R}_j A}|} \, .$$

- N_0 denotes the number of unit cells in the crystal

- N denotes the number of electrons per unit cell
- M is the number of nuclei per unit cell
- $Z_{\vec{R}_j A} \equiv Z_A$ stands for the charge of nucleus A in unit cell $\vec{R}_j$
- $|\vec{r}_i - \vec{r}_j|$ is the distance between the i-th and the j-th electron
- $|\vec{r}_i - \vec{r}_{\vec{R}_j A}|$ is the distance between the i-th and the A-th nucleus in unit cell $\vec{R}_j$

Hartree-Fock is still not a satisfactory approximation and there are dozends of post-Hartree-Fock methods in quantum chemistry to improve on this starting point.

3 Correlated Band Structures

3.1 Green's Function in Blochorbitals

The Green's function in terms of Blochorbitals

$$G_{pq}(\vec{k}, t, t') = (-\mathrm{i})\ \langle \Psi_0^N |\, \hat{T}[\hat{c}_{\vec{k}p}(t)\, \hat{c}^\dagger_{\vec{k}q}(t')]\, | \Psi_0^N \rangle\ ,$$

is well-suited for a correlated treatment of band structures as the bands are given by the poles of $G_{pq}(\vec{k}, \omega)$. We use an approximation scheme for the Green's function which is complete up to n-th order, the algebraic diagrammatic construction scheme.

The explicit evaluation of $G_{pq}(\vec{k}, \omega)$ in terms of Blochorbitals involves, as most correlation methods do, excited intermediate

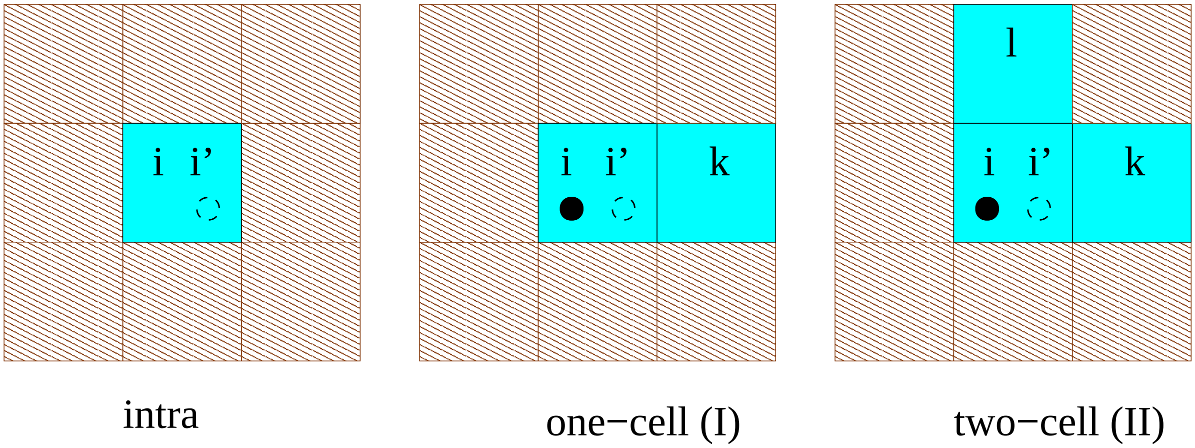

Figure 1: Incremental scheme for intracell increments.

configurations. For band structures these are ionized determinants, also called configuration state functions, which constitute the configuration space: $1h$, $1p$, $2h1p$, $3h2p$, …

The number of reciprocal space integrations scales with the number of individual Hartree-Fock holes/particles, eg. $2h1p \geq 3$, $3h2p \geq 5$, …

To carry out the reciprocal space integration the Brioullin zone must be discretized using a Monkhorst-Pack net [1].

As this mesh is composed of thousands of $\vec{k}$-points one is urged to minimize the number of integrations.

3.2 Direct Space

Luckily correlation effects turn out to be fairly local in direct space. In fact, ground states of crystals can be described even by small clusters of atoms or molecules. Therefore Wannier orbitals are a natural starting point.

We apply a Wannier transformation to the one-particle Bloch orbital $|\vec{k}\nu\rangle$

$$|\vec{R}\nu\rangle = \frac{1}{\sqrt{N_0}} \sum_{\vec{k}\in\mathrm{B.Z.}} \mathrm{e}^{-\mathrm{i}\vec{k}\vec{R}} \, |\vec{k}\nu\rangle \ .$$

Since Marzari and Vanderbilts work [2] there is a well-defined recipe to generate maximally localized Wannier functions.

Dilemma: On the one hand we want to use direct space quantities to describe electron correlation. On the other hand band structures are defined with respect to reciprocal space.

This problem can be addressed by using semitransformed quantities where just a suitable quantity is transformed to reciprocal space after evaluation in direct space. We use the self-energy for this purpose.

This means, the band structre is obtained by solving the Dyson equation

$$\boldsymbol{G}(\vec{k},\omega) = \boldsymbol{G}^0(\vec{k},\omega) + \boldsymbol{G}^0(\vec{k},\omega)\,\boldsymbol{\Sigma}(\vec{k},\omega)\,\boldsymbol{G}(\vec{k},\omega) \ .$$

The self-energy can be transformed easily

$$\boldsymbol{\Sigma}(\vec{k},\omega) = \sum_{\vec{R}} \mathrm{e}^{i\vec{k}\vec{R}} \, \boldsymbol{\Sigma}(\vec{R},\omega) \ .$$

Up to know we have reformulated the problem conveniently. As a crystal is huge we cannot simply build up all possible configuration state functions and then diagonalize the Hamiltonian within this new basis. This would correspond to full CI. We must use the periodicity!

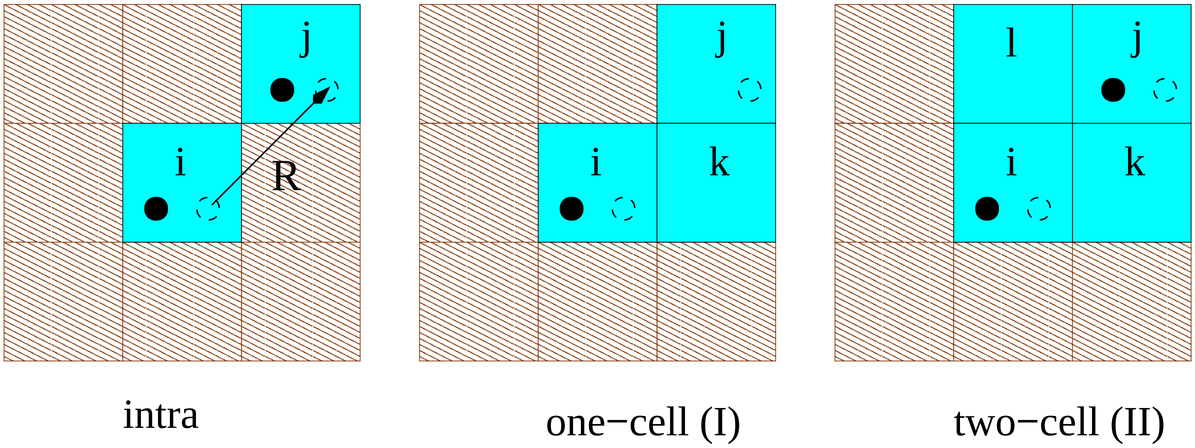

Figure 2: Incremental scheme for intercell increments.

3.3 Configuration Selection

Configuration selection is an issue that originates from configuration interaction calculations in molecules. There one tries to shrink the configuration space by selecting only those configurations which have an appreciable effect on the correlation energy. Although Green's functions are quite different from CI we can use this idea but have to search for an appropriate selection criterion.

The analytic expression of the second order self-energy diagram

$$D^{+(2)}_{nm}(\vec{R},\omega) \;=\; \frac{V_{\vec{0}n\,\vec{R}_1j\,[\vec{R}_2k\,\vec{R}_3l]}\,V^{*}_{\vec{R}m\,\vec{R}_1j\,[\vec{R}_2k\,\vec{R}_3l]}}{\omega+\varepsilon_{\vec{R}_1j}-\varepsilon_{\vec{R}_2k}-\varepsilon_{\vec{R}_3l}} \times n_{\vec{R}_1j}\,\bar{n}_{\vec{R}_2k}\,\bar{n}_{\vec{R}_3l}$$

can be used for determining a minimal or flat configuration space. There the decay of the product of the Coulomb integrals has to be monitored with distance. Selecting an appropriate threshold yields a decent cutoff criterion. This "flattening" of the configuration space also yields a correlation method which scales linearly with the number of atoms in the unit cell.

We would like to remark that the dissociation of a molecule, Mott's Metal insulator transition and many other effects on the correlation due to the variation of the internuclear distances are concerned with such a local treatment of electron correlation.

4 Outlook

The four essential ingredients for our treatment are

- Hartree-Fock approximation
- Direct space quantities
- Algebraic diagrammatic construction
- Configuration selection

Using the Hartree-Fock approximation and Green's functions for correlated ab initio band structures for insulators and semiconductors, we improve the description of (perfect) crystals extremely. This enables us to describe

- Hydrogen bonded systems
- The breakdown of the one-particle picture of ionization (The ionization process yields also an excitation of the system, in other words $2h1p$- and $2p1h$-configurations couple strongly to the one-particle states.)

References

[1] H. J. Monkhorst and J. D. Pack, Special Points for Brillouin-Zone Integrations, Phys. Rev. B **13**, 5188–5192 (1976).

[2] N. Marzari and D. Vanderbilt, Maximally Localized Generalized Wannier Functions for Composite Energy Bands, Phys. Rev. B **56**, 12847–12865 (1997).