Calculations of band structures

using wave-function based correlation methods

Elke Pahl

Centre of Theoretical Chemistry and Physics
Institute of Fundamental Sciences
Massey University Auckland
New Zealand

- Uwe Birkenheuer (Forschungszentrum Rossendorf)

- Peter Fulde (MPIPKS Dresden)

- Hermann Stoll (Universitaet Stuttgart)

- Liviu Hozoi (MPIPKS Dresden)

- Peter Schwerdtfeger (Massey University)
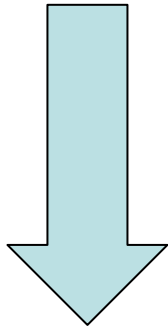
Introduction

- HF band structures of solid/ extended systems can be obtained more or less routinely (e.g. CRYSTAL)

- Calculations beyond Hartree Fock including electron correlation effects are very difficult

- Two approaches:
  - **DFT**: problems in systematic improvement
  - **wave-function based methods**: desirable! well-developed quantum-chemical methods exist which allow for systematic improvement

Introduction

- Band structures are hard ! because we have to deal with:

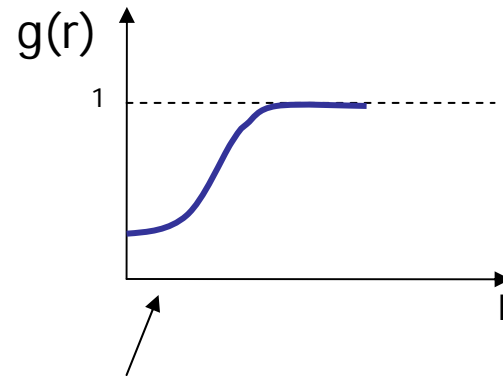 - extended states
  - ionic states
  - excited states

Key idea

- Electron correlation is a local property!

Pair distribution function
for homogeneous electron gas

Use local picture

- cluster approach for correlation calculation
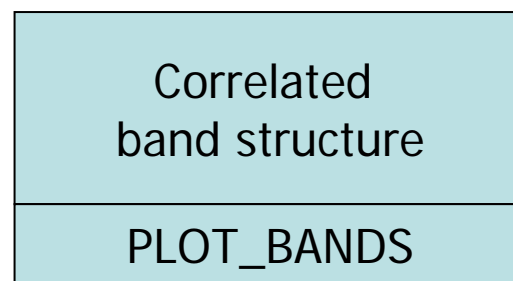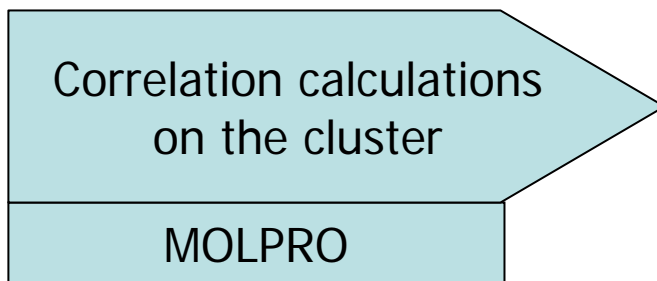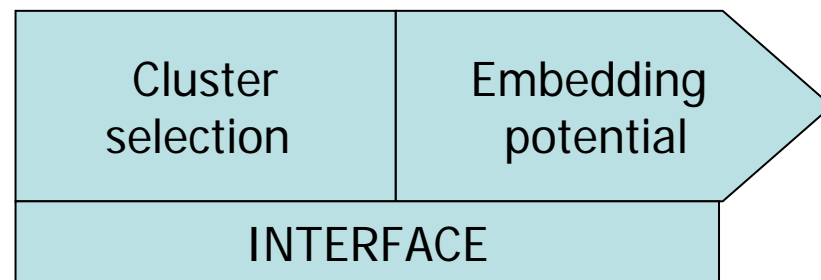
- make use of localized orbitals

exchange hole: Pauli principle

correlation hole: Coulomb repulsion

Introduction

Aim: wave-function based *ab initio* correlation calculations of band structures

HF calculation on the infinite system	Localization: Wannier functions
CRYSTAL	

Cluster selection	Embedding potential
INTERFACE	

Correlation calculations on the cluster
MOLPRO

Correlated band structure
PLOT_BANDS
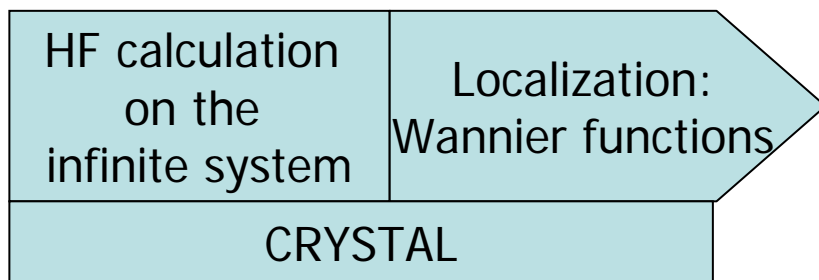
Overview

1) Localization:

   Wannier function, band disentanglement

2) Cluster selection and Embedding

3) Correlation calculation:

   Frozen local hole approximation:

      - theoretical background

      - application to simple examples

Wannier functions

- Bloch waves: $\psi_{\mathbf{k}\nu}(\mathbf{r}) = u_{\mathbf{k}\nu}(\mathbf{r}) \, e^{i\mathbf{k}\mathbf{r}} \, \boxed{e^{i\tilde{\Phi}_\nu(\mathbf{k})}}$

   (extended)

   arbitrary phase

- Wannier functions: $\tilde{\varphi}_{\mathbf{R}\nu}(\mathbf{r}) = \dfrac{V}{(2\pi)^3} \displaystyle\int_{\mathcal{BZ}} \psi_{\mathbf{k}\nu}(\mathbf{r}) \, e^{-i\mathbf{k}\mathbf{R}} \, \boxed{e^{i\Phi(\mathbf{k})}} \; d\mathbf{k}$

   (localized)

- provide chemical, intuitive picture of electronic structure of cluster
- localized functions $\Rightarrow$ post-Hartree Fock electron correlation

Wannier functions

• generalized Wannier functions:

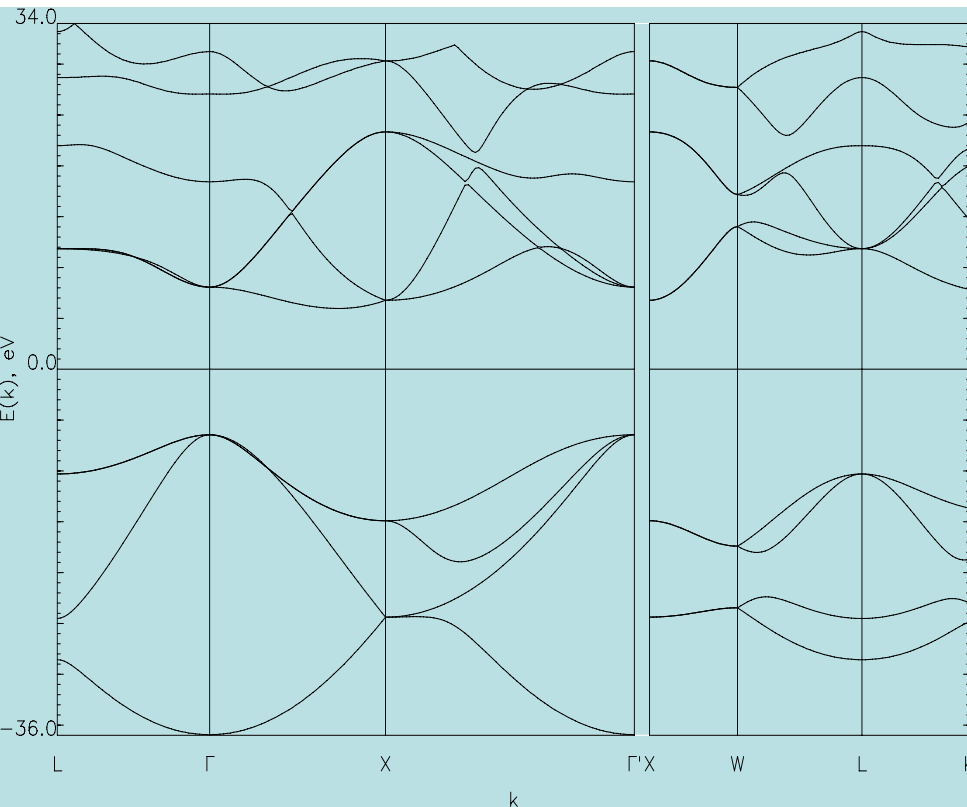for group of N bands separated by energy gap from rest over entire Brioullin zone

$$\varphi_{\mathbf{R}n}(\mathbf{r}) = \frac{V}{(2\pi)^3} \int\limits_{\mathcal{BZ}} [\sum_{\nu=1}^{N} U_{\nu n}(\mathbf{k})\, \psi_{\mathbf{k}\nu}(\mathbf{r})] \quad e^{i\mathbf{k}\mathbf{R}}\, d\mathbf{k}$$

Problem:

• Scheme can only be applied to isolated band complexes

• In particular unoccupied Bloch waves do not exhibit
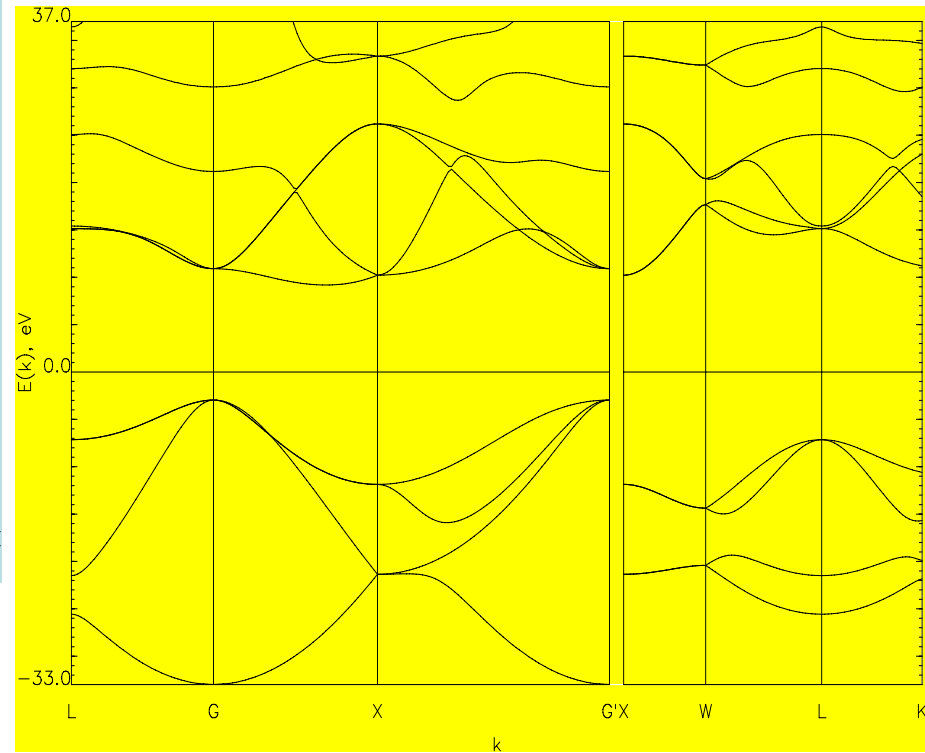
needed band gaps

Band disentanglement

HF band structure of diamond

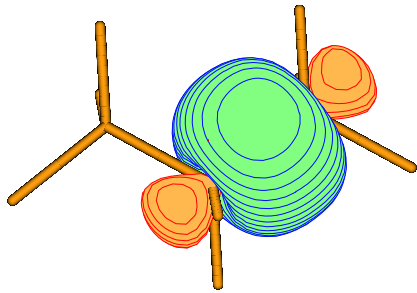
without d basis functions

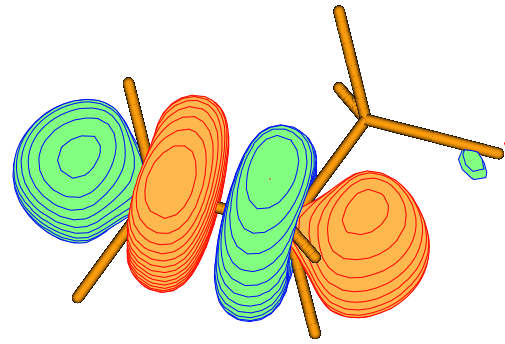vdz basis

Massey University

Localized Wannier functions

Example: diamond C_{11} cluster

HOMO

LUMO

Massey University

Cluster selection

Example: diamond

C_8

C_{11}

C_{14} cis

C_{14} trans
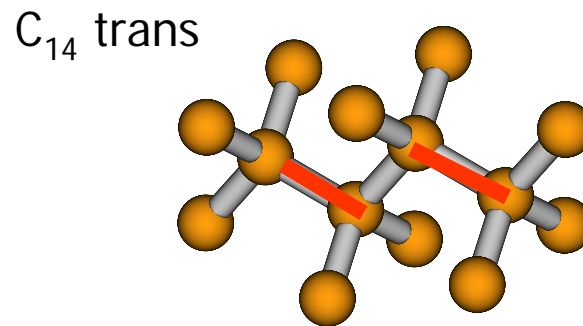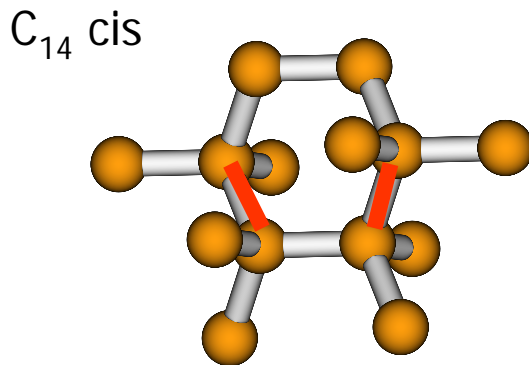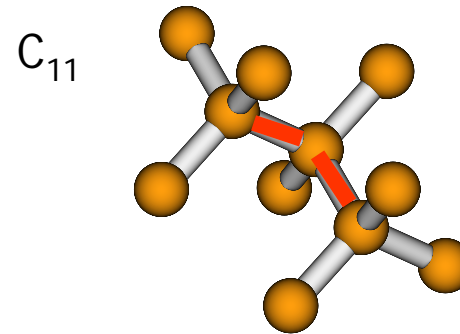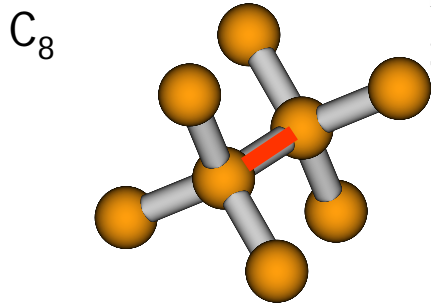
Construction of **new orbital space**
for the subsequent correlation calculation

1) Generation of projected Wannier orbitals

$$|w'_{\mathbf{R}n}\rangle = \mathcal{P}|w_{\mathbf{R}n}\rangle$$

$$\text{with} \quad \mathcal{P} = \sum |\xi_\nu\rangle(S^{-1})_{\nu\mu}\langle\xi_\mu|$$

S: overlap matrix of cluster basis functions $|\xi_\nu\rangle$

Selection of proj. WO's: all core orbitals in cluster, all occupied and

virtual orbitals inside cluster and on dangling bonds

2) Construction of compact projected atomic orbitals (PAO's) from basis

functions $|\xi_\nu\rangle$ of active region

3) Filling orbitals to arrive at complete set of orthonormal orbitals

(equals number of basis functions in cluster)

Embedding potential

One can include the influence of the frozen environment on the electrons in the active region of the cluster by a one-particle contribution V_{emb} which is added to the molecular Hamiltonian in the subsequent correlation calculations

$$V_{\text{emb}} = F_{\text{solid}} - F_{\text{clus}}[P_{\text{solid}}(C)]$$

$$P_{\text{solid}}(C) = 2 \sum_{\mathbf{R}n \in C}^{occ} |w_{\mathbf{R}n}\rangle\langle w_{\mathbf{R}n}|$$

F_{solid}: Fock matrix of the solid

P_{solid}: density matrix of all localized occupied Wannier orbitals

assigned to the cluster C

Correlation calculation

starting point: neutral Hartree Fock ground state $|\Phi_{\mathrm{HF}}^{N}\rangle = \dfrac{1}{N} det(|\phi_i\rangle)$

$|\phi_i\rangle \in$ {proj. WO's, ... }

reference states: correlated states

cationic states: $\quad\quad |\Phi_i^{N-1}\rangle = \hat{c}_i |\Phi_{\mathrm{HF}}^{N}\rangle$ $\quad\quad\quad\quad\quad |\Psi_i^{N-1}\rangle$
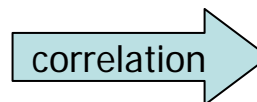
correlation

anionic states: $\quad\quad |\Phi_i^{N+1}\rangle = \hat{c}_i^{\dagger} |\Phi_{\mathrm{HF}}^{N}\rangle$ $\quad\quad\quad\quad\quad |\Psi_i^{N+1}\rangle$

standard correlation methods can be used like CI (configuration interaction) and CC (coupled cluster) methods

BUT: these methods become easily computationally too expensive $\Longrightarrow$ further approximations are needed !

Correlated band structure

Band energies can be recovered by diagonalizing the **k** dependent 'ionization potential' and 'electron affinity' matrices, $I_{nn'}(\mathbf{k}) \text{ and } A_{nn'}(\mathbf{k})$:

$$I_{nn'}(\mathbf{k}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} I_{nn'}(\mathbf{R}) \quad \text{with}$$

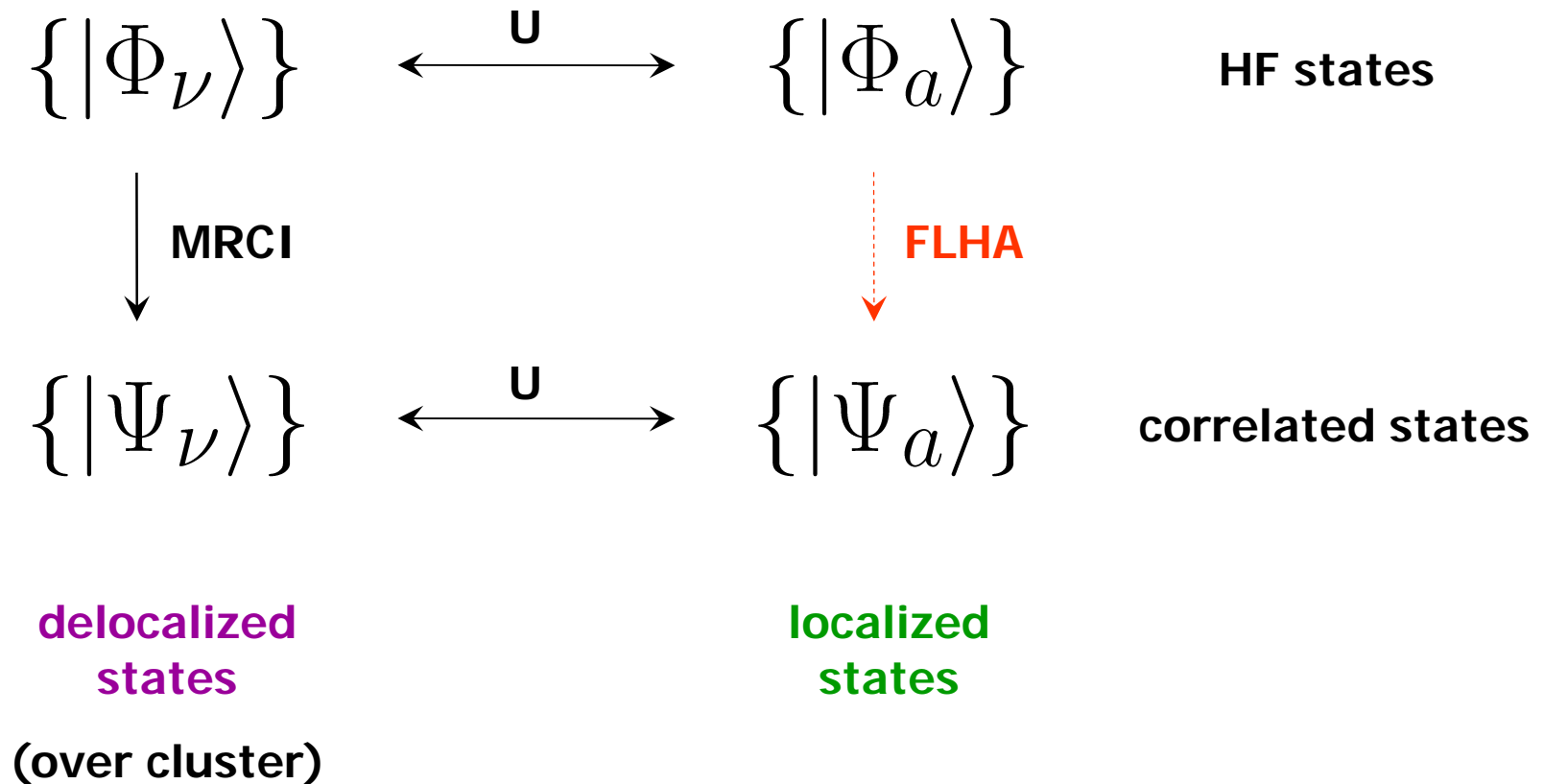$$I_{nn'}(\mathbf{R}) = \langle \Psi_{\mathbf{0}n\sigma}^{N-1} | H | \Psi_{\mathbf{R}n'\sigma}^{N-1} \rangle - E^N \delta_{\mathbf{0}\mathbf{R}} \delta_{nn'}$$

$$A_{mm'}(\mathbf{k}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} A_{mm'}(\mathbf{R}) \quad \text{with}$$

$$A_{nn'}(\mathbf{R}) = E^N \delta_{\mathbf{0}\mathbf{R}} \delta_{mm'} - \langle \Psi_{\mathbf{0}m\sigma}^{N+1} | H | \Psi_{\mathbf{R}m'\sigma}^{N+1} \rangle$$

Theoretical Background

Frozen Local Hole Approximation

$$\{|\Phi_\nu\rangle\} \xleftrightarrow{\ \textbf{U}\ } \{|\Phi_a\rangle\} \qquad \textbf{HF states}$$

$$\downarrow \textbf{MRCI} \qquad\qquad\qquad \textcolor{red}{\downarrow \textbf{FLHA}}$$

$$\{|\Psi_\nu\rangle\} \xleftrightarrow{\ \textbf{U}\ } \{|\Psi_a\rangle\} \qquad \textbf{correlated states}$$

delocalized states   **localized states**
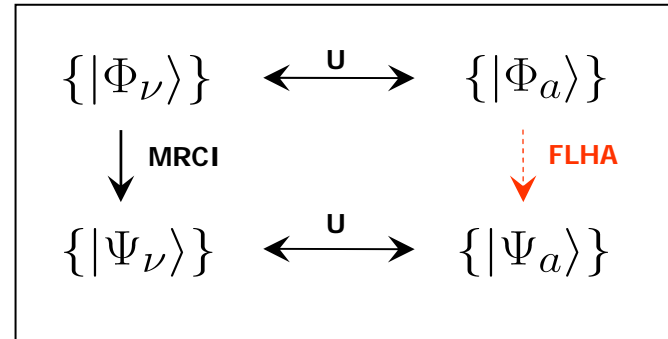
(over cluster)

Theoretical Background
Frozen Local Hole Approximation

- generation of approximate
  correlated local hole states CLHS's $|\tilde{\Psi}_a\rangle$:

    separate correlation calculation for each
    reference state $|\Phi_a\rangle$ in which the
    localized orbital $|a\rangle$ is kept frozen

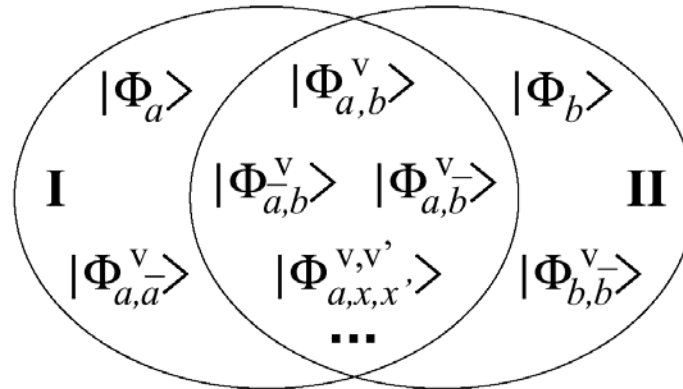   this implies a <u>configuration selection</u>

Example: CI(SD) calculation:

$$|\tilde{\Psi}_a\rangle = \alpha_a|\Phi_a\rangle + \underset{x,v}{\Sigma}\, \alpha_{a,x}^{v}|\Phi_{a,x}^{v}\rangle + \underset{x,x',v,v'}{\Sigma}\, \alpha_{a,x,x'}^{v,v'}|\Phi_{a,x,x'}^{v,v'}\rangle$$

$x, x' \in \{\bar{a}, b, \bar{b}, ...\}$ $\bar{a}$: electron with opposite spin to removed electron
v, v' virtual orbitals

Diagram (top right):

$\{|\Phi_\nu\rangle\} \quad \xleftrightarrow{\ \text{U}\ } \quad \{|\Phi_a\rangle\}$

$\downarrow$ MRCI   FLHA (dashed arrow)

$\{|\Psi_\nu\rangle\} \quad \xleftrightarrow{\ \text{U}\ } \quad \{|\Psi_a\rangle\}$

Theoretical Background
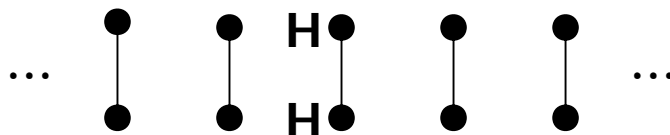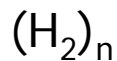
Frozen Local Hole Approximation

1. *configuration spaces* for different hole states $|\tilde{\Psi}_a\rangle$ are *overlapping* :

2. approximated CLHS's $|\tilde{\Psi}_a\rangle$ are *not orthogonal* $\implies$

   a generalized eigenvalue problem has to be solved

Correlated band structures
MPIPKS, 2007

Massey University

Applications

1. H$_2$ chains   (H$_2$)$_n$

van der Waals binding between H$_2$ units in the neutral chain
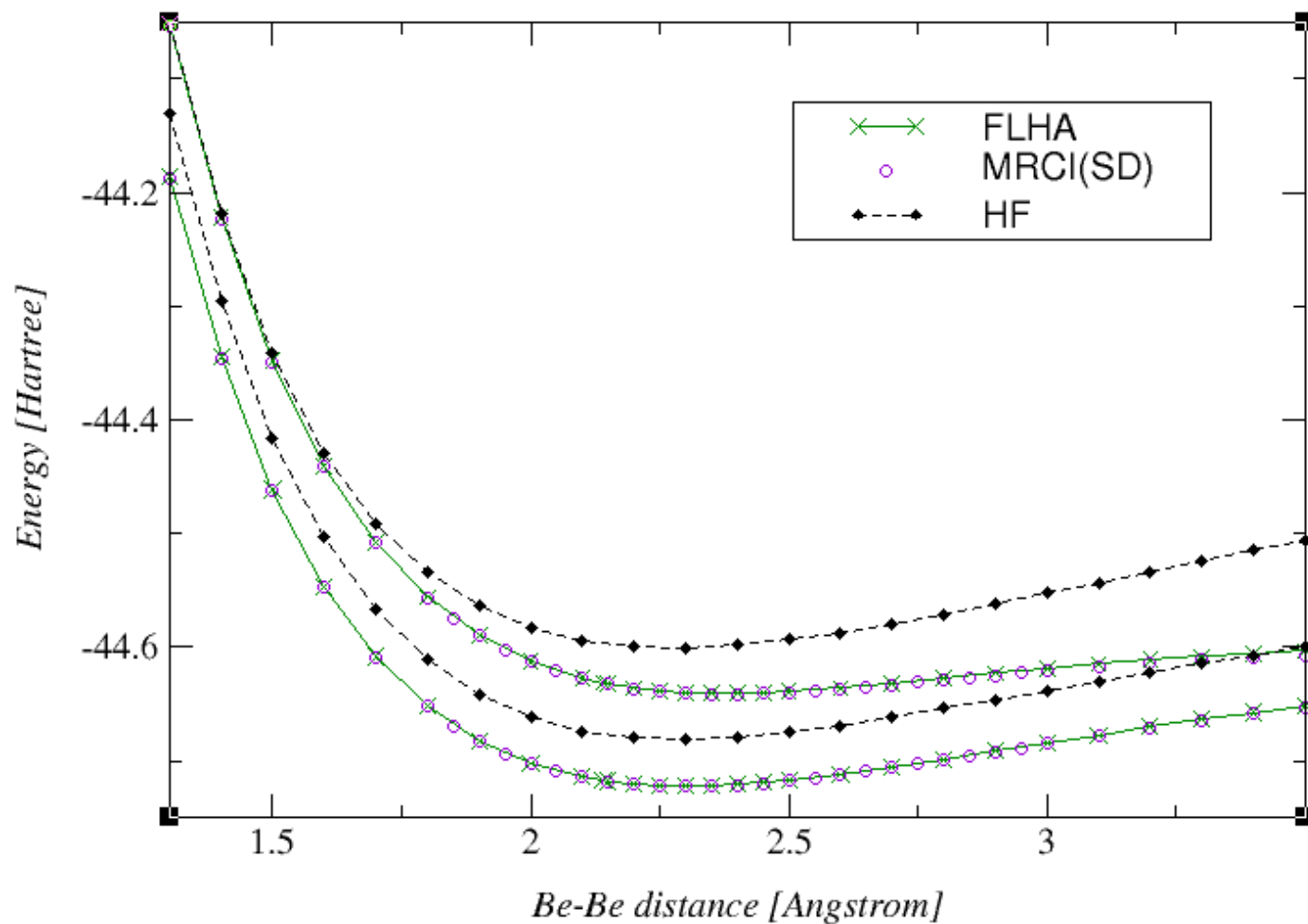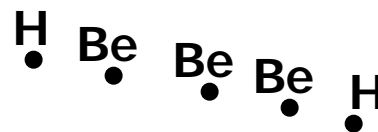
2. Be chains   H-(Be)$_n$-H

predominately covalently bound ground state

Technical details: - calculations performed with MOLPRO

- approximation compared to complete MRCI(SD) calculation

- Foster-Boys localization

H-Be₃-H

basis set: s cc-p VDZ

Perturbation analysis

<u>Quasi-degenerate variational perturbation theory</u>:

partitioning into model space $\mathcal{M}$ (spanned by HF hole configurations) and orthogonal complement, $\hat{P}$ and $\hat{Q}$ being the corresponding projectors, i.e. $\hat{P} + \hat{Q} = \hat{1}$

$$|\Psi_\nu\rangle \quad \text{: correlated wave function}$$

$$|\Psi_\nu^{\mathcal{M}}\rangle = \hat{P}|\Psi_\nu\rangle$$

define wave operator $\hat{\Omega}$: $\qquad |\Psi_\nu\rangle = \hat{\Omega}|\Psi_\nu^{\mathcal{M}}\rangle$

Perturbation analysis

H_0 consists only of diagonal elements $F_{ii} = \varepsilon_i$

perturbation contains the non-diagonal elements F_{ij}
as well as the usual two- and one-electron contributions

$\langle ij||kl \rangle$ and $\displaystyle\sum_a^{occ} \langle ia||ja \rangle$

wave operator in 1st order:

$$\hat{\Omega} = \sum_c |\Phi_c\rangle\langle\Phi_c|$$

$$+ \sum_c \sum_{a<b,v} |\Phi_{ab}^v\rangle \frac{\langle vc||ab\rangle}{\varepsilon_v - \varepsilon_a - \varepsilon_b + \varepsilon_c} \langle \Phi_c|$$

Perturbation analysis

H_0 consists only of diagonal elements $F_{ii}=\varepsilon_i$

perturbation contains the non-diagonal elements F_{ij}
as well as the usual two- and one-electron contributions
$\langle ij||kl\rangle$ and $\displaystyle\sum_a^{\text{occ}}\langle ia||ja\rangle$

wave operator in 1$^{\text{st}}$ order:

$$\hat{\Omega} = \sum_c |\Phi_c\rangle\langle\Phi_c|$$

$$+ \sum_c \sum_{a<b,v} |\Phi_{ab}^v\rangle \frac{\langle vc||ab\rangle}{\varepsilon_v - \varepsilon_a - \varepsilon_b + \varepsilon_c}\langle\Phi_c|$$

$$+ \sum_c \sum_{a<b,v<w} |\Phi_{abc}^{vw}\rangle \frac{\langle vw||ab\rangle}{\epsilon_v + \epsilon_w - \epsilon_a - \epsilon_b}\langle\Phi_c|$$

Perturbation analysis

$$\hat{\Omega} = \sum_c |\Phi_c\rangle\langle\Phi_c|$$

$$+ \sum_c \sum_{a<b,v} |\Phi_{ab}^v\rangle \frac{\langle vc||ab\rangle}{\varepsilon_v - \varepsilon_a - \varepsilon_b + \varepsilon_c}\langle\Phi_c|$$

$$+ \sum_c \sum_{a<b,v<w} |\Phi_{abc}^{vw}\rangle\frac{\langle vw||ab\rangle}{\epsilon_v + \epsilon_w - \epsilon_a - \epsilon_b}\langle\Phi_c|$$

$$\hat{\Omega}^{\mathrm{FLH}}(h) = |\Phi_h\rangle\langle\Phi_h| + \sum_{a\neq h,v} |\Phi_{ah}^v\rangle \frac{\langle vh||ah\rangle}{\varepsilon_v - \varepsilon_a}\langle\Phi_h|$$

$$+ \sum_{a<b,v<w} |\Phi_{abh}^{vw}\rangle\frac{\langle vw||ab\rangle}{\epsilon_v + \epsilon_w - \epsilon_a - \epsilon_b}\langle\Phi_h|$$

$$\hat{\Omega} = \sum_h \hat{\Omega}^{\mathrm{FLH}}(h) + \hat{\Pi}$$

Perturbation analysis

$$\hat{\Pi} = \sum_{a<b,v} \sum_{c \notin \{a,b\}} |\Phi_{ab}^v\rangle \frac{\langle vc||ab\rangle}{\varepsilon_v - \varepsilon_a - \varepsilon_b + \varepsilon_c} \langle \Phi_c|$$

$\Longrightarrow$ **only contributions with three distinct occupied spin orbitals are neglected**

FLHA at a glance

- FLHA is two-step procedure:

    1. Wave-function based correlation calculations are performed to find correlation holes around frozen local hole

    2. Effective Hamiltonian matrix is constructed and diagonalized; hole can delocalize and form proper Bloch state

- It was shown – numerically and by perturbation theory – that the FLHA performs very well

- In an analogue manner the method can be applied to anionic electron attachment states

- Further simplification possible by treating the N§1 states with a frozen local hole on Hartree-Fock level only

Conclusions and Outlook

Correlated band structures can be obtained by using wave-function based *ab initio* methods!

Projects:

- correlated band structure of diamond and silicon

  by using the FLHA

- treatment of ionic substances like MgO ($\rightarrow$ Liviu Hozoi)

Massey University
COLLEGE OF SCIENCES

Te Kunenga
Ki Pūrehuroa

Courses start February 2008!

Study Postgraduate Mathematical Physics at Massey University Auckland

MSc and BSc(Hons)

Students will take courses in core areas of Mathematical Physics such as quantum mechanics, field theory and general relativity as well as special topics on cutting-edge physics from active researchers.

Students will engage in original research under the supervision of members of the Institute of Fundamental Sciences and the Institute of Information and Mathematical Sciences.

Topics include

Quantum Gases
Nonperturbative Field Theory
Nonlinear Phenomena
Hadronic Physics
Computational Physics

For more information view web site at **http://mathphys.massey.ac.nz**.