Fock-space multi-reference coupled cluster method

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Outline

- Coupled cluster (CC) method: exponential Ansatz
- Multireference (MR) approach: basic definitions (model space, wave operator, effective Hamiltonian)
- Exponential form of the MR wave operator = multireference coupled cluster (MRCC) method
- Fock space (FS) realization of the MRCC theory:
  - a) sector structure of the model space
  - b) amplitude equations for the particular sectors
  - c) crucial point: iterative solving of the FS-MRCC equations
- Fundamental drawback of the standard FS-MRCC approach: diverging solutions

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Outline - continued

- Remedy: replacement of the iterative scheme with the diagonalization of the intermediate Hamiltonian (IH) matrix
- Construction of the IH matrix via canonical Bloch equation (CBE)
- Wide range of applications of the FS-MRCC approach in the IH formalism:
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  - excitation energies
  - ionization potentials
  - electron affinities
- IH-FS-MRCC as a useful tool in theoretical spectroscopy
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Coupled cluster (CC) method

exponential parametrization of the wave function

$$\mathbf{|\Psi_o\rangle = e^{T}|\Phi_o\rangle}$$

$$\mathbf{T \;=\; T_1 + T_2 + T_3 ... + T_N}$$

where

$$\mathbf{T_n \;=\; (n!)^{-2}\Sigma_{ab...}\Sigma_{ij...}t_{ij...}^{ab...}a^{\dagger}b^{\dagger}...ji}$$

Coupled cluster (CC) method

- amplitude equation:

$$\langle \mathbf{\Phi^{ab\ldots}_{ij\ldots}} | \mathbf{e^{-T} H e^{T}} | \mathbf{\Phi_o} \rangle = \langle \mathbf{\Phi^{ab\ldots}_{ij\ldots}} | \mathbf{\bar{H}} | \mathbf{\Phi_o} \rangle = \mathbf{0}$$

- energy expression:

$$\mathbf{E} \;=\; \langle \mathbf{\Phi_o} | \mathbf{e^{-T} H e^{T}} | \mathbf{\Phi_o} \rangle = \langle \mathbf{\Phi_o} | \mathbf{\bar{H}} | \mathbf{\Phi_o} \rangle$$

where $\mathbf{\bar{H}}$ – similarity transformed Hamiltonian.

Single reference CC method

Single reference calculations

$$\mathbf{H\Psi = E\Psi}$$

H – Hamiltonian operator to be diagonalized in large configurational space (size: milions, bilions, ...)

Multireference CC method

Multireference solution

$$\mathbf{H}_{\mathrm{eff}}\boldsymbol{\Psi}^{\mathbf{o}} = \mathbf{E}\boldsymbol{\Psi}^{\mathbf{o}}$$

$\mathbf{E}$ – the same eigenvalue

$\mathbf{H}_{\mathrm{eff}}$ – effective Hamiltonian (complicated operator) to be diagonalized within small configurational subspace (model space with P projector, size: tens, hundreds, ...)

Multireference CC method

MULTIREFERENCE FORMALISM

Model space: $\mathrm{M_o}$ $\quad \mathrm{P}$

Orthogonal space: **M** $\quad \mathrm{Q}$

$$\Psi_k^o \;=\; P\Psi_k = \sum_{m}^{m_o} c_{mk}\Phi_m$$

Important quantity: wave operator Ω

$$\Psi_k \;=\; \Omega\Psi_k^o$$

recovers the exact wave function from the model one.

Multireference CC method

Ω operator is found by solving Bloch equation

$$\mathrm{H\Omega P = \Omega PH\Omega P}$$

Energy E is found by diagonalizing of effective Hamiltonian

$$\mathrm{H_{eff} \;=\; PH\Omega P}$$

Multireference Fock space CC method

Model space $\equiv$ **valence Fock space**

Valence Fock space is a configurational space consisting of:

- *0 valence quasiparticle:*
- *1 valence quasiparticle:*
  - 1 valence hole
  - 1 valence particle
- *2 valence quasiparticles:*
  - 2 valence holes
  - 1 valence hole, 1 valence particle
  - 2 valence particles

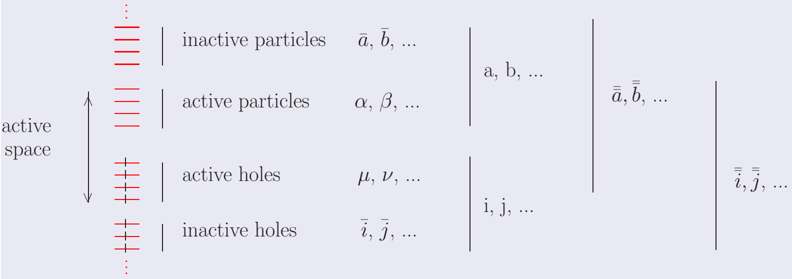
Multireference Fock space CC method

Active space vs. model space

Active space is defined by the number of active particle levels and active hole levels.

Multireference Fock space CC method

Classifications of the one-electron levels



inactive particles $\bar{a}, \bar{b}, \ldots$

active particles $\alpha, \beta, \ldots$

active holes $\mu, \nu, \ldots$

inactive holes $\bar{i}, \bar{j}, \ldots$

a, b, ...

i, j, ...

$\bar{\bar{a}}, \bar{\bar{b}}, \ldots$

$\bar{\bar{i}}, \bar{\bar{j}}, \ldots$

active space

$$\Sigma_{\bar{\bar{a}}} = \Sigma_a + \Sigma_\mu$$

$$\Sigma_{\bar{\bar{i}}} = \Sigma_i + \Sigma_\alpha$$

Multireference Fock space CC method

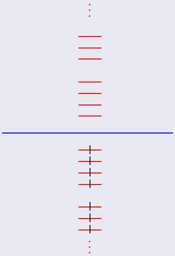
Active space vs. model space

Model space: spanned by the configurations generated by the excitations within active levels.

Model space is divided into sectors.

Multireference Fock space CC method

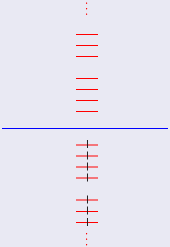
Fermi vacuum



Multireference Fock space CC method

0 valence quasiparticle

(0,0) sector

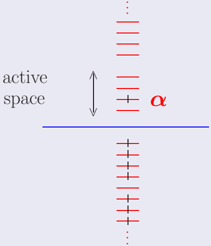


Ground state

Multireference Fock space CC method

1 valence particle
(1,0) sector

$\mathbf{\Phi}_\alpha$



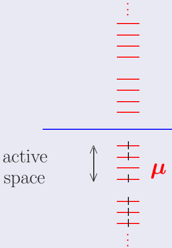
Single electron attached states

Multireference Fock space CC method

1 valence hole

(0,1) sector

$\boldsymbol{\Phi}_\mu$



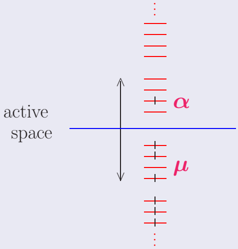
Singly ionized states

Multireference Fock space CC method

1 valence particle and 1 valence hole

(1,1) sector

$$\mathbf{\Phi}_{\mu}^{\alpha}$$



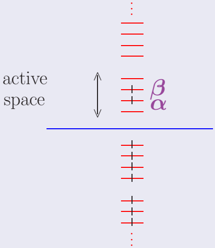
Excited states

Multireference Fock space CC method

2 valence particles

(2,0) sector

$\mathbf{\Phi}^{\alpha\beta}$



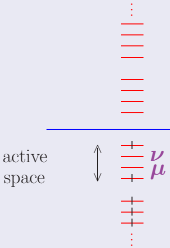
Double electron attached states

Multireference Fock space CC method

2 valence holes

(0,2) sector

$\boldsymbol{\Phi}_{\mu\nu}$



Doubly ionized states

Multireference Fock space CC method

Important step: definition of the Fock space wave operator

Wave operator: $\mathbf{\Omega = \{e^{\tilde{S}^{(k,l)}}\}P}$

k – number of valence particles

l – number of valence holes

$\{\quad\}$ – normal ordering

P – model space projector

$\mathbf{\tilde{S}^{(k,l)}}$ is responsible for excitations from model space to orthogonal one.

Multireference Fock space CC method

Cluster structure of the wave operator

$$\mathbf{\tilde{S}^{(k,l)} = \tilde{S}_1^{(k,l)} + \tilde{S}_2^{(k,l)} + \cdots + \tilde{S}_n^{(k,l)}}$$

Definition of the $\tilde{S}_n^{(k,l)}$ *operator*

$$\mathbf{\tilde{S}_n^{(k,l)} = \frac{1}{(n!)^2} \Sigma'_{\bar{\bar{a}}\bar{\bar{b}}\cdots\overline{\overline{ij}}\cdots} s^{\bar{\bar{a}}\bar{\bar{b}}\cdots}_{\overline{\overline{ij}}\cdots} \{\bar{\bar{a}}^\dagger \bar{\bar{b}}^\dagger \cdots \overline{\overline{ji}}\}}$$

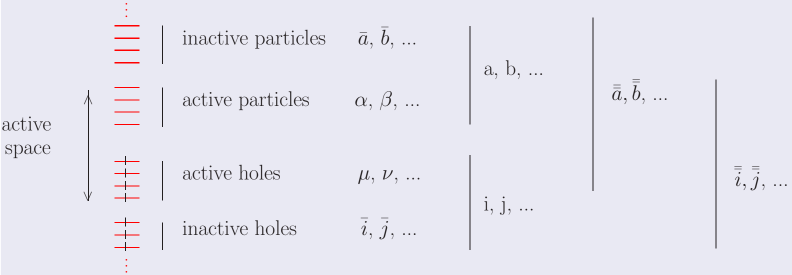
$\prime$ – excitations within model space excluded

$s^{\bar{\bar{a}}\bar{\bar{b}}\cdots}_{\overline{\overline{ij}}\cdots}$ – sought amplitudes (coefficients)

$\bar{\bar{a}}^\dagger \bar{\bar{b}}^\dagger \cdots \overline{\overline{ji}}$ – creation-annihilation operators

Multireference Fock space CC method

Classifications of the one-electron levels



$$\Sigma_{\bar{\bar{a}}} = \Sigma_a + \Sigma_\mu$$

$$\Sigma_{\bar{\bar{i}}} = \Sigma_i + \Sigma_\alpha$$

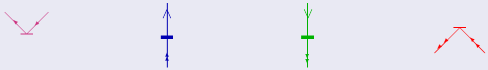
Multireference Fock space CC method

Sector structure of the $\tilde{\mathrm{S}}_\mathrm{n}$ operator

$$\tilde{\mathrm{S}}_1 = \sum_{\bar{\bar{\mathbf{a}}}\bar{\bar{\mathbf{i}}}}{}' \{ \mathbf{s}^{\bar{\bar{\mathbf{a}}}}_{\bar{\bar{\mathbf{i}}}} \bar{\bar{\mathbf{a}}}^\dagger \bar{\bar{\mathbf{i}}} \}$$

$$= \sum_{\mathbf{ai}} \{ \mathbf{s}^{\mathbf{a}}_{\mathbf{i}} \mathbf{a}^\dagger \mathbf{i} \} + \sum_{\bar{\mathbf{a}}\alpha} \{ \mathbf{s}^{\bar{\mathbf{a}}}_{\alpha} \bar{\mathbf{a}}^\dagger \alpha \} + \sum_{\mu\bar{\mathbf{i}}} \{ \mathbf{s}^{\mu}_{\bar{\mathbf{i}}} \mu^\dagger \bar{\mathbf{i}} \} + \sum_{\mu\alpha} \{ \mathbf{s}^{\mu}_{\alpha} \mu^\dagger \alpha \}$$

$$= \mathbf{S}_1^{(0,0)} + \mathbf{S}_1^{(1,0)} + \mathbf{S}_1^{(0,1)} + \mathbf{S}_1^{(1,1)}$$



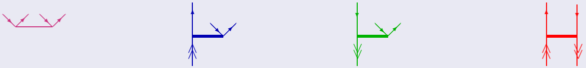
Multireference Fock space CC method

Sector structure of the $\tilde{\mathbf{S}}_{\mathbf{n}}$ operator

$$\tilde{\mathbf{S}}_2 = \frac{1}{4}\sum_{\bar{\bar{a}}\bar{\bar{b}}\bar{\bar{i}}\bar{\bar{j}}}{}'\{s^{\bar{\bar{a}}\bar{\bar{b}}}_{\bar{\bar{i}}\bar{\bar{j}}}\bar{\bar{a}}^\dagger\bar{\bar{b}}^\dagger\bar{\bar{j}}\bar{\bar{i}}\}$$

$$= \frac{1}{4}\sum_{abij}\{s^{ab}_{ij}a^\dagger b^\dagger ji\} + \frac{1}{2}\sum_{ab\alpha j}\{s^{ab}_{\alpha j}a^\dagger b^\dagger j\alpha\} + \frac{1}{2}\sum_{\mu bij}\{s^{\mu b}_{ij}\mu^\dagger b^\dagger ji\} + \sum_{\mu\alpha bj}{}'\{s^{\mu b}_{\alpha j}\mu^\dagger b^\dagger j\alpha\} + \cdots$$

$$= \mathbf{S}_2^{(0,0)} + \mathbf{S}_2^{(1,0)} + \mathbf{S}_2^{(0,1)} + \mathbf{S}_2^{(1,1)} + \cdots$$



with the terms for the sectors (2,0), (0,2), (2,1), (1,2) and (2,2) are skipped and in the definition of the $S_2^{(1,1)}$ operator the case where the both creation lines are active is excluded

Multireference Fock space CC method

Sector structure of the $\tilde{S}^{(k,l)}$ *operator*

$$\mathbf{\tilde{S}^{(k,l)} \;=\; \Sigma_{i=0}^{k}\Sigma_{j=0}^{l}S^{(i,j)}}$$

$$\mathbf{\tilde{S}^{(1,1)} = S^{(0,0)} + S^{(1,0)} + S^{(0,1)} + S^{(1,1)}}$$

$$\mathbf{S^{(0,0)} = T}$$

Multireference Fock space CC method

Fock space equations are obtained by introduction just defined Ω operator

$$\mathbf{\Omega} = \{\mathbf{e}^{\tilde{\mathbf{S}}^{(\mathbf{k},\mathbf{l})}}\}$$

into the Bloch equation:

$$H\Omega P = \Omega\,\underbrace{PH\Omega P}_{H_{eff}}$$

Multireference Fock space CC method

The general FS-CC equation for the (k, l) sector formulated in the operator form can be written as:

$$\mathbf{H}\{\mathbf{e}^{\tilde{\mathbf{S}}^{(\mathbf{k,l})}}\}\mathbf{P}^{(\mathbf{k,l})} \;=\; \{\mathbf{e}^{\tilde{\mathbf{S}}^{(\mathbf{k,l})}}\}\mathbf{P}^{(\mathbf{k,l})}\mathbf{H}_{\mathbf{eff}}^{(\mathbf{k,l})}\mathbf{P}^{(\mathbf{k,l})} \qquad (1)$$

It is convenient to separate from the $\tilde{\mathrm{S}}$ the operator corresponding to the (0,0) sector:

$$\tilde{\mathbf{S}}^{(\mathbf{k,l})} \;=\; \mathbf{S}^{(\mathbf{0,0})} + \tilde{\tilde{\mathbf{S}}}^{(\mathbf{k,l})} = \mathbf{T} + \tilde{\tilde{\mathbf{S}}}^{(\mathbf{k,l})} \qquad (2)$$

Rewriting Eq. (1) on the basis of the equality in Eq. (2) and multiplying from the left with e^{-T} we obtain:

$$\mathbf{e}^{-\mathbf{T}}\mathbf{H}\mathbf{e}^{\mathbf{T}}\{\mathbf{e}^{\tilde{\tilde{\mathbf{S}}}^{(\mathbf{k,l})}}\}\mathbf{P}^{(\mathbf{k,l})} \;=\; \{\mathbf{e}^{\tilde{\tilde{\mathbf{S}}}^{(\mathbf{k,l})}}\}\mathbf{P}^{(\mathbf{k,l})}\mathbf{H}_{\mathbf{eff}}^{(\mathbf{k,l})}\mathbf{P}^{(\mathbf{k,l})}$$

Multireference Fock space CC method

The final form of the FS-CC equation is obtained upon projection of the last equation on the excited determinants in each sector represented by the projector $\mathbf{Q}^{(\mathbf{k},\mathbf{l})}$ and remembering that $\mathbf{e}^{-\mathbf{T}}\mathbf{H}\mathbf{e}^{\mathbf{T}} = \bar{\mathbf{H}}$:

$$\mathbf{Q}^{(\mathbf{k},\mathbf{l})}\bar{\mathbf{H}}\{\mathbf{e}^{\tilde{\bar{\mathbf{S}}}^{(\mathbf{k},\mathbf{l})}}\}\mathbf{P}^{(\mathbf{k},\mathbf{l})} = \mathbf{Q}^{(\mathbf{k},\mathbf{l})}\{\mathbf{e}^{\tilde{\bar{\mathbf{S}}}^{(\mathbf{k},\mathbf{l})}}\}\mathbf{P}^{(\mathbf{k},\mathbf{l})}\mathbf{H}_{\mathbf{eff}}^{(\mathbf{k},\mathbf{l})}\mathbf{P}^{(\mathbf{k},\mathbf{l})}$$

whereas the model space projection produces $\mathbf{H}_{\mathbf{eff}}$

$$\mathbf{P}^{(\mathbf{k},\mathbf{l})}\mathbf{H}_{\mathbf{eff}}\mathbf{P}^{(\mathbf{k},\mathbf{l})} = \mathbf{P}^{(\mathbf{k},\mathbf{l})}\bar{\mathbf{H}}\{\mathbf{e}^{\tilde{\bar{\mathbf{S}}}^{(\mathbf{k},\mathbf{l})}}\}\mathbf{P}^{(\mathbf{k},\mathbf{l})}$$

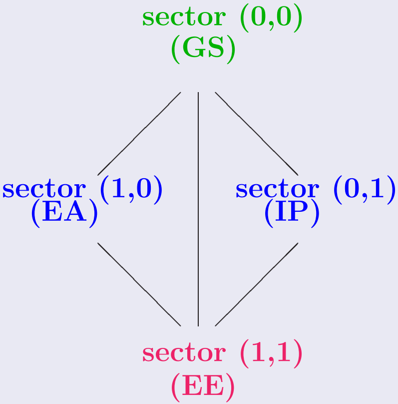
Multireference Fock space CC method

Hierarchical solving of the FS-CC equations:

1. solving of the (0,0) sector
2. solving of the (1,0) and (0,1) sectors
3. solving of the (1,1) sector

Multireference Fock space CC method

Hierarchy of the FS solutions
EE calculations



sector (0,0)
(GS)

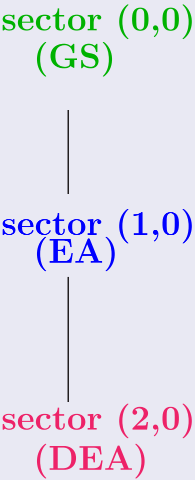
sector (1,0)
(EA)

sector (0,1)
(IP)

sector (1,1)
(EE)

Multireference Fock space CC method

Hierarchy of the FS solutions: DEA calculations



sector (0,0)
(GS)

sector (1,0)
(EA)

sector (2,0)
(DEA)

Multireference Fock space CC method

Hierarchy of the FS solutions: DIP calculations

sector (0,0)
(GS)

sector (0,1)
(IP)

sector (0,2)
(DIP)

Multireference Fock space CC method

Steps in the Fock space calculations:
e.g. (2,0) sector

1. solve the (0,0) sector (i.e. single reference CC)
2. construct $\bar{H}$ elements using converged T amplitudes
3. solve iteratively the (1,0) sector constructing in each iteration $H_{eff}^{(1,0)}$
4. if (1,0) sector done solve iteratively equations for the (2,0) sector constructing in each iteration $H_{eff}^{(2,0)}$
5. once amplitude got converged diagonalize the $\mathbf{H}_{\mathbf{eff}}^{(\mathbf{2,0})}$ matrix to obtain the sought eigenvalues

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Multireference Fock space CC method

The FS-CC method described here is usually referred to as a standard or H_{eff} based scheme.

The characteristic feature of it is an iterative solving of the FS-CC equations.

IMPORTANT FS-CC PAPERS

- D. Mukherjee, R. K. Moitra, A. Mukhopadhyay, *Mol. Phys.*, **30**, 1861 (1975).
- I. Lindgren, *Int. J. Quantum Chem. Symp.*, **12**, 33 (1978).
- M. Haque, D. Mukherjee, *J. Chem. Phys.*, **80**, 5058 (1984).
- D. Mukherjee, *Chem. Phys. Lett.*, **125**, 207 (1986).
- S. Pal, M. Rittby, R. J. Bartlett, D. Sinha, D. Mukherjee, *J. Chem. Phys.*, **88**, 4357 (1988).
- U. Kaldor, *Int. J. Quantum Chem. Symp.*, **20**, 445 (1986)

Multireference Fock space CC method

Fundamental problems of the standard FS-CC method

- intruder states
- diverging solutions $\equiv$ convergence difficulties

Multireference Fock space CC method

New approach to the FS-CC theory

Intermediate Hamiltonian (IH) formalism provides the way to avoid troublesome iterative procedure of the FS problems

Iterative FS scheme $\equiv$ diagonalization of the IH matrix

Multireference Fock space CC method

Bloch equation in the diagonalization of the $\bar{\mathbf{H}}_{\mathbf{SD}}$ matrix in the subspace of singly and doubly excited configurations

$$\bar{\mathbf{H}}_{\mathbf{SD}} = \mathbf{e}^{-(\mathbf{T_1}+\mathbf{T_2})}\mathbf{H}\mathbf{e}^{\mathbf{T_1}+\mathbf{T_2}}$$

Multireference Fock space CC method

Matrix eigenvalue problem

$$\bar{\mathrm{H}}\mathrm{C} = \mathrm{C}\mathrm{E}$$

Partition Technique (PT)

$$\begin{bmatrix} \bar{\mathrm{H}}_{\mathrm{PP}} & \bar{\mathrm{H}}_{\mathrm{PQ}} \\ \bar{\mathrm{H}}_{\mathrm{QP}} & \bar{\mathrm{H}}_{\mathrm{QQ}} \end{bmatrix} \begin{bmatrix} \mathrm{C}_{\mathrm{P}} \\ \mathrm{C}_{\mathrm{Q}} \end{bmatrix} = \begin{bmatrix} \mathrm{C}_{\mathrm{P}} \\ \mathrm{C}_{\mathrm{Q}} \end{bmatrix} \mathrm{E}_{\mathrm{P}}$$

Multireference Fock space CC method

$$\begin{aligned}
\mathbf{\bar{H}_{PP}C_P + \bar{H}_{PQ}C_Q} &= \mathbf{C_P E_P} \\
\mathbf{\bar{H}_{QP}C_P + \bar{H}_{QQ}C_Q} &= \mathbf{C_Q E_P}
\end{aligned}$$

Multiplying both equations from the right with $\mathbf{C_P^{-1}}$ we obtain:

$$\begin{aligned}
\mathbf{\bar{H}_{PP} + \bar{H}_{PQ}C_Q C_P^{-1}} &= \mathbf{C_P E_P C_P^{-1}} \\
\mathbf{\bar{H}_{QP} + \bar{H}_{QQ}C_Q C_P^{-1}} &= \mathbf{C_Q C_P^{-1} C_P E_P C_P^{-1}}
\end{aligned}$$

Multireference Fock space CC method

Defining:

$$\begin{aligned}\mathbf{H_{eff}} &= \mathbf{C_P E_P C_P^{-1}} \\ \mathbf{S_Q} &= \mathbf{C_Q C_P^{-1}}\end{aligned}$$

we may rewrite the equations

$$\begin{aligned}\mathbf{\bar{H}_{PP} + \bar{H}_{PQ} C_Q C_P^{-1}} &= \mathbf{C_P E_P C_P^{-1}} \\ \mathbf{\bar{H}_{QP} + \bar{H}_{QQ} C_Q C_P^{-1}} &= \mathbf{C_Q C_P^{-1} C_P E_P C_P^{-1}}\end{aligned}$$

as

$$\begin{aligned}\mathbf{\bar{H}_{PP} + \bar{H}_{PQ} S_Q} &= \mathbf{H_{eff}} \\ \mathbf{\bar{H}_{QP} + \bar{H}_{QQ} S_Q - S_Q H_{eff}} &= \mathbf{0}\end{aligned}$$

Multireference Fock space CC method

The eigenvalue equation for iterative solving

$$\begin{aligned}
\mathbf{H_{eff}} &= \mathbf{\bar{H}_{PP}} + \mathbf{\bar{H}_{PQ} S_Q} \\
-\mathbf{\bar{H}^{d}_{QQ} S_Q} &= \mathbf{\bar{H}_{QP}} + \mathbf{\bar{H}'_{QQ} S_Q} - \mathbf{S_Q H_{eff}} \\
\mathbf{\bar{H}_{QQ}} &= \mathbf{\bar{H}^{d}_{QQ}} + \mathbf{\bar{H}'_{QQ}}
\end{aligned}$$

$\mathbf{\bar{H}_{PP}}$ - constant contribution to the effective Hamiltonian

$\mathbf{\bar{H}_{PQ} S_Q}$ - contribution from $\mathbf{S_Q}$ to $\mathbf{H_{eff}}$

$\mathbf{\bar{H}_{QP}}$ - constant contribution to $\mathbf{S_Q}$

$\mathbf{\bar{H}^{d}_{QQ}}$ - diagonal part of $\mathbf{\bar{H}_{QQ}}$

$\mathbf{\bar{H}'_{QQ} S_Q}$ - nondiagonal part of $\mathbf{\bar{H}_{QQ}}$ operating on vector $\mathbf{S_Q}$

Multireference Fock space CC method

Diagrammatic representation

$-\bar{H}^{d}_{QQ}S_{Q}$

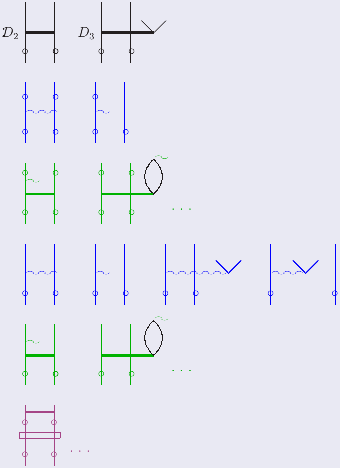
$\bar{H}_{PP}$:

$\bar{H}_{PQ}S_{Q}$:

$\bar{H}_{QP}$:

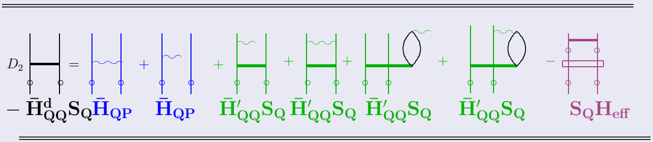
$\bar{H}'_{QQ}S_{Q}$:

$S_{Q}H_{eff}$:



Multireference Fock space CC method

EOM-CCSD via canonical Bloch equation



Multireference Fock space CC method

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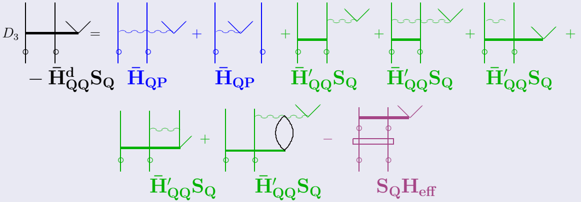
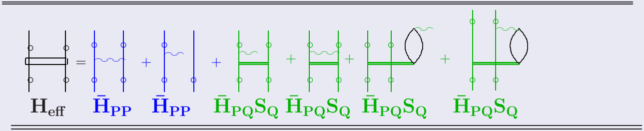


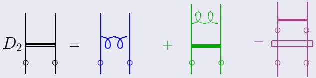
EOM-CCSD via canonical Bloch equation



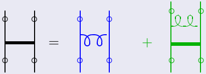
Multireference Fock space CC method

Diagrammatic canonical Bloch equation in compact form for the EOM-CC problem

$$-\bar{\mathbf{H}}^{\mathbf{d}}_{\mathbf{QQ}}\mathbf{S}_{\mathbf{Q}} = \bar{\mathbf{H}}_{\mathbf{QP}} + \bar{\mathbf{H}}'_{\mathbf{QQ}}\mathbf{S}_{\mathbf{Q}} - \mathbf{S}_{\mathbf{Q}}\mathbf{H}_{\mathbf{eff}}$$



$$\mathbf{H}_{\mathbf{eff}} = \bar{\mathbf{H}}_{\mathbf{PP}} + \bar{\mathbf{H}}_{\mathbf{PQ}}\mathbf{S}_{\mathbf{Q}}$$



Multireference Fock space CC method

In general the form of the Bloch Equation (BE) depends on the form of the wave operator Ω. Here we constructed the simplest BE with the purpose to diagonalize the matrix.

We call this BE a Canonical Bloch Equation (CBE).

Multireference Fock space CC method

Hence, if we have the Bloch equation in the CBE form we may replace the tedious iterative solving of the Bloch equation with the direct diagonalization of the matrix.

Multireference Fock space CC method

The question is:

Can we rewrite the Fock space equations in such a way that they assume the CBE form ?

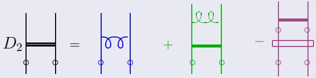
If so, we would be able to replace the (frequently diverging) iterative scheme with diagonalization of a certain properly constructed matrix.

The answer is **YES**

Multireference Fock space CC method

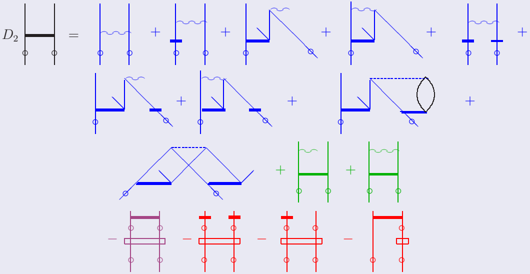
GOAL:

TO REORGANIZE THE FS-CC EQUATIONS IN THE (1,1) SECTOR IN SUCH A WAY THAT IT CAN BE REPLACED BY DIAGONALIZING THE MODIFIED HAMILTONIAN MATRIX IN THE CONFIGURATIONAL SUBSPACE



Multireference Fock space CC method

The diagrammatic representation in skeleton form of the FS S$_2$ equation for the (1,1) sector at the CCSD level in standard formulation



Multireference Fock space CC method

In order to bring the standard FS equations into the CBE form it is enough to do the following transformation, i.e. replacing the $\mathbf{S_2^{(1,1)}}$ operator with $\mathbf{\bar{S}_2^{(1,1)}}$:

$$\mathbf{\bar{S}_2^{(1,1)}} = \mathbf{S_2^{(1,1)}} + \mathbf{S_1^{(0,1)}}\mathbf{S_1^{(1,0)}} + \mathbf{S_1^{(0,1)}}\mathbf{E^{(1,0)}} + \mathbf{S_1^{(1,0)}}\mathbf{E^{(0,1)}}$$

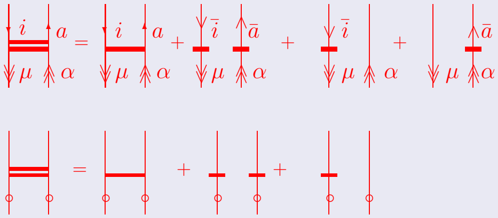
$$\mathbf{E^{(1,0)}} = \sum_{\alpha}\{\alpha^{\dagger}\alpha\} \qquad \mathbf{E^{(0,1)}} = \sum_{\mu}\{\mu^{\dagger}\mu\}$$

or for amplitudes:

$$\mathbf{\bar{S}_{i\alpha}^{\mu a}} = \mathbf{S_{i\alpha}^{\mu a}} + \mathbf{S_{i}^{\mu}}\mathbf{S_{\alpha}^{\bar{a}}} + \mathbf{S_{i}^{\mu}}\delta_{\alpha\mathbf{a}} + \delta_{\mu\mathbf{i}}\mathbf{S_{\alpha}^{\bar{a}}}$$

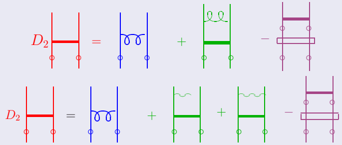
Multireference Fock space CC method

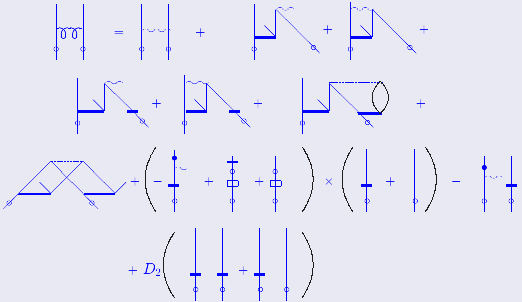
In diagrammatic form it looks like:



Multireference Fock space CC method

Diagrammatic, canonical form of the FS $\mathbf{S}_{\mathbf{2}}^{(\mathbf{1},\mathbf{1})}$ equation at the CCSD level





Multireference Fock space CC method

Replacement of S_2 with $\bar{\mathrm{S}}_2$ made it possible to bring the FS equation into canonical Bloch equation form

Multireference Fock space CC method

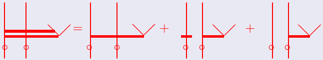
IH-FS-CCSDT (1,1) variant

Multireference Fock space CC method

We replace $\mathbf{S}_3^{(1,1)}$ with $\bar{\mathbf{S}}_3^{(1,1)}$:

$$\bar{\mathbf{S}}_3^{(1,1)} = \mathbf{S}_3^{(1,1)} + \mathbf{S}_1^{(0,1)}\mathbf{S}_2^{(1,0)} + \mathbf{S}_1^{(1,0)}\mathbf{S}_2^{(0,1)} + \mathbf{S}_2^{(0,1)}\mathbf{E}^{(1,0)} + \mathbf{S}_2^{(1,0)}\mathbf{E}^{(0,1)}$$

which diagrammatically can be expressed as:



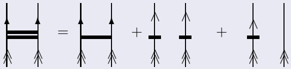
Multireference Fock space CC method

IH-FS-CCSD (2,0) variant

Multireference Fock space CC method

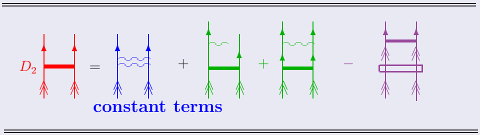
IH-FS-CCSD for DEA

Amplitude transformation for the $S_2^{(2,0)}$ cluster operator



Multireference Fock space CC method

IH-FS-CCSD for DEA



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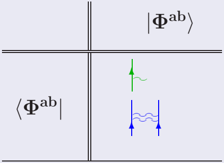
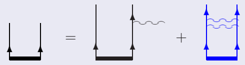
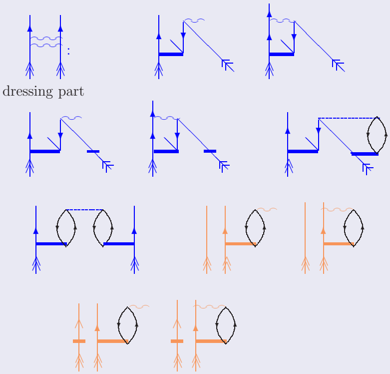


Structure of the matrix to be diagonalized

Multireference Fock space CC method

IH-FS-CCSD for DEA





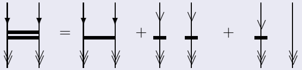
Multireference Fock space CC method

IH-FS-CCSD (0,2) variant

Multireference Fock space CC method

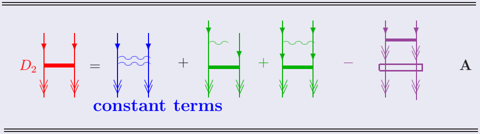
IH-FS-CCSD for DIP

Amplitude transformation for the $S_2^{(0,2)}$ cluster operator



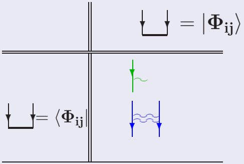
Multireference Fock space CC method

IH-FS-CCSD for DIP



⇓

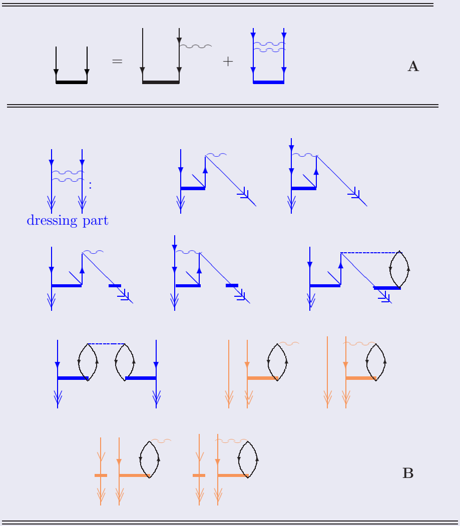
Structure of the matrix to be diagonalized



B

Multireference Fock space CC method

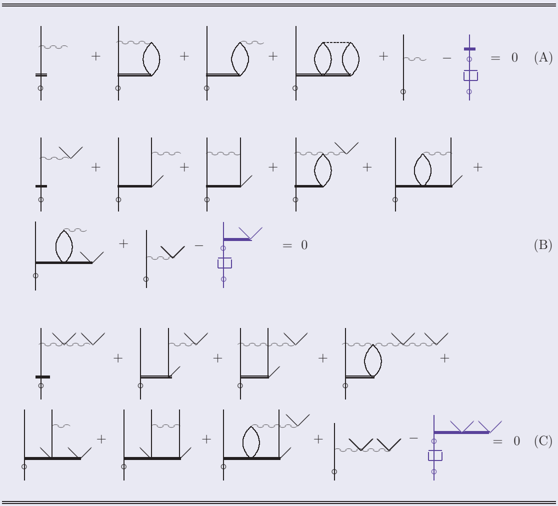
IH-FS-CCSD for DIP



Multireference Fock space CC method

FS-CCSD (1,0) and (0,1) variants

FS-CCSD for EA and IP



Multireference Fock space CC method

Standard FS equations for the one valence sectors are in CBE form !

Hence, we may replace the iterative solving with the diagonalization of the EOM matrix.

Conclusion

IP(EA)-EOM-CC gives identically the same results as FS-CC (0,1)((1,0)) method.

RELEVANT IH PAPERS

- J.-P. Malrieu, Ph. Durand, J.-P. Daudey, *J. Phys. B*, **18**, 809 (1985) – *IH for perturbation theory*

- L. Meissner, R. J. Bartlett, *J. Chem. Phys.*, **102**, 7490 (1995) – *IH for FS-CCSD (1,1)*
- L. Meissner, *J. Chem. Phys.*, **108**, 9227 (1998) – *IH for FS-CCSD (1,1)*

- M. Musiał, R. J. Bartlett, *J. Chem. Phys.*, **129**, 134105 (2008) – *IH for FS-CCSDT (1,1)*

- M. Musiał, R. J. Bartlett, *J. Chem. Phys.*, **135**, 044121 (2011) – *IH for FS-CCSD (0,2)*

- M. Musiał, *J. Chem. Phys.*, **136**, 134111, (2012). – *IH for FS-CCSD (2,0)*

RELEVANT REVIEWS

- D. Mukherjee, S. Pal,
  Adv. Quantum Chem., **20**, 292 (1989).
- R. J. Bartlett, M. Musiał,
  Rev. Mod. Phys., **79**, 291 (2007).
- D. I. Lyakh, M. Musiał, V. Lotrich,
  R. J. Bartlett,
  Chem. Rev., **112**, 182 (2012).

Multireference Fock space CC method

APPLICATIONS

Multireference Fock space CC method

Potential energy curves for the alkali metal diatomics

with FS-CCSD (2,0) method based on the RHF(restricted Hartree-Fock) reference function.

Standard way for alkali diatomics is full CI for two valence electrons with all inner electrons replaced with effective potential (FCI=CISD)

Double electron attached states

- DEA: double electron attachment

$$\mathbf{A \Longrightarrow A^{-2}}$$

$$\mathbf{DEA = E_A - E_{A^{-2}}}$$

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- In our case:

Reference function: $\mathbf{A^{+2}}$

DEA calculations: $\mathbf{A}$

Double electron attached states

- DEA: double electron attachment

$$\mathbf{A} \Longrightarrow \mathbf{A}^{-2}$$

$$\mathbf{DEA} = \mathbf{E_A} - \mathbf{E_{A^{-2}}}$$

- In our case:

Reference function: $\mathbf{A}^{+2}$

DEA calculations: $\mathbf{A}$

$$\mathbf{A}^{+2} \quad \overrightarrow{\mathbf{DEA}} \quad \mathbf{A}$$

DEA example: calculation of PECs for the $\mathrm{Na_2}$ molecule

- Neutral molecule

$$\mathrm{Na_2}$$

$$\dot{\mathbf{Na}} \text{ ——— } \ldots\ldots \text{ ——— } \dot{\mathbf{Na}}$$

- Double ionized molecule

$$\mathrm{Na_2^{+2}}$$

$$\mathbf{Na}^{+} \text{ —— } \ldots\ldots \text{ —— } \mathbf{Na}^{+}$$

$\mathrm{Na_2^{+2}}$ system separates into two closed shell subunits (isoelectronic with Ne atom). Very convenient reference function.

Multireference Fock space CC method

IH-FS-CCSD (2,0) for DEA

- GS part, i.e. (0,0) sector: $T = T_1 + T_2$ (scaling $n^6(n_o^2 n_v^4)$)
- EA part, i.e. (1,0) sector: $S = S_1 + S_2$ (scaling $n^5(n_o^1 n_v^4)$)
- DEA part, i.e. (2,0) sector: $S = S_2$ (scaling $n^5(n_o^2 n_v^3)$)

Nonstandard DEA applications for alkali metal diatomics

Prescription for the correct generation of the PEC

1. remove two electrons from the AB molecule
2. do the RHF calculations for the AB^{+2} system
3. for the AB^{+2} system do the correlated calculations with the DEA type method: FS-CCSD (2,0) (capable to accurately describe the electronic states resulting from the attachment of a pair of electrons to the reference)
4. do such calculations for all interatomic distances

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4. do such calculations for all interatomic distances

RESULTS

DEA calculations: Li_2

Li_2 molecule

- Basis set: uncontracted ANO-RCC with additional two diffuse functions for s, p, d, f shells (228 basis functions)
- model space: 7396 configurations

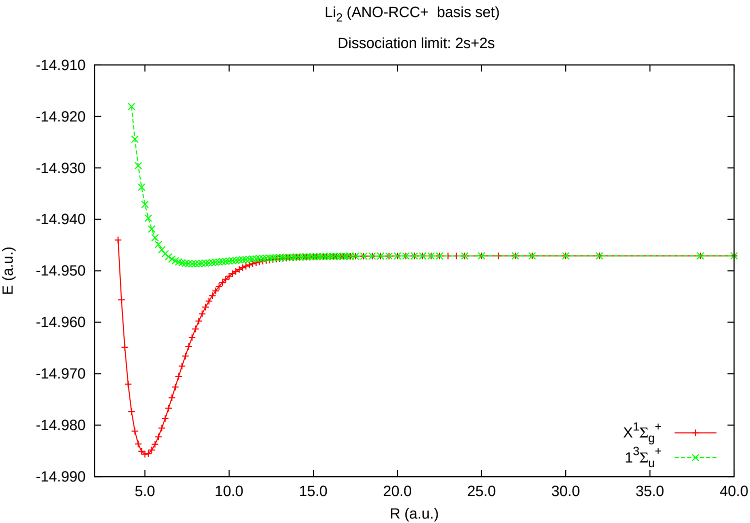
DEA calculations: Li_2

Potential energy curves for 34 electronic states dissociating into the following asymptotic limits:

2s+2s	2 states	(2)
2s+2p	8 states	(12)
2s+3s	4 states	(4)
2p+2p	12 states	(18)
2s+3p	8 states	(12)

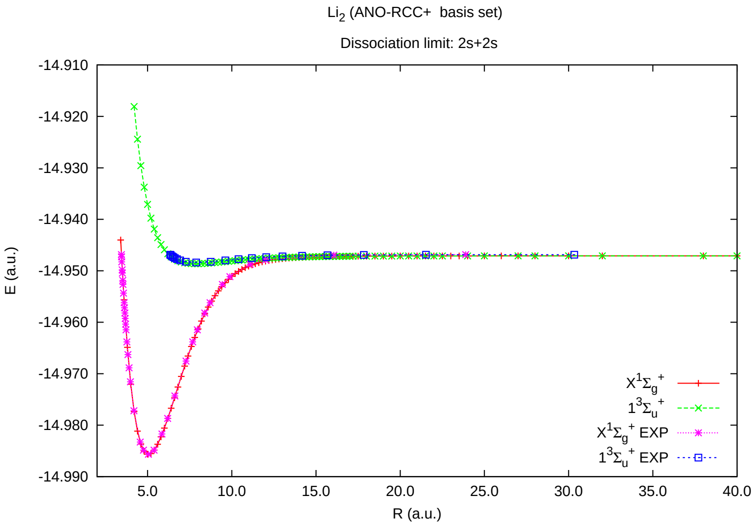
DEA calculations: PECs of Li_2

Dissociation limit: 2S+2S



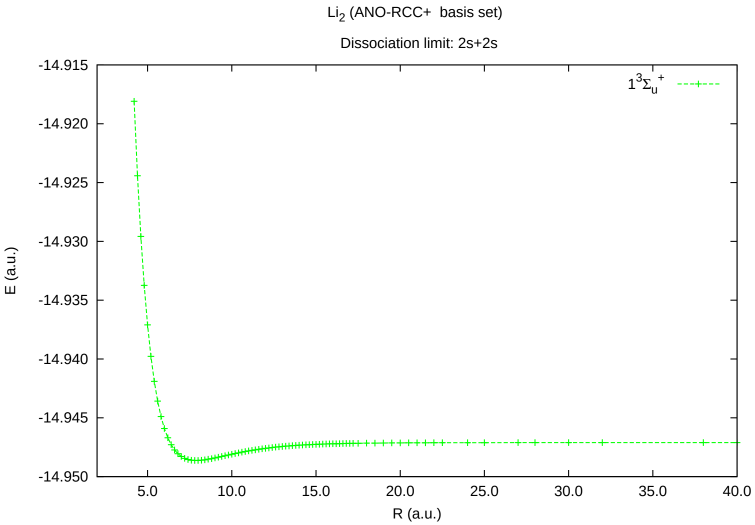
DEA calculations: PECs of Li_2

Dissociation limit: 2S+2S – comparison with experiment



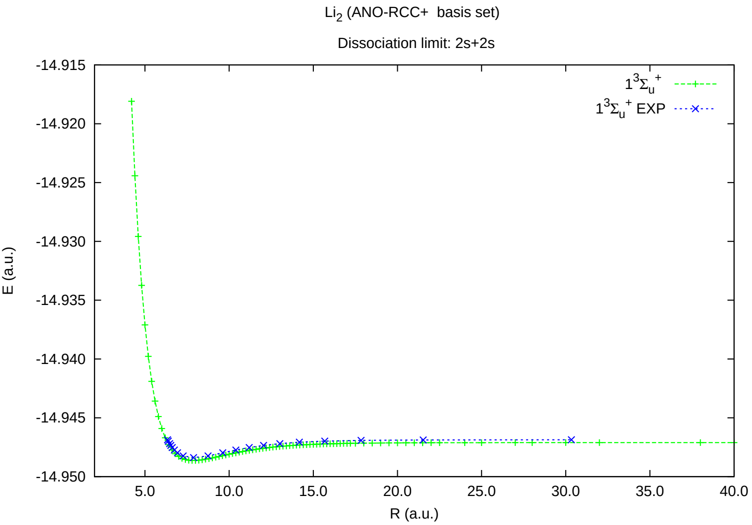
DEA calculations: PECs of Li_2

$1^3\Sigma_u^+$ state



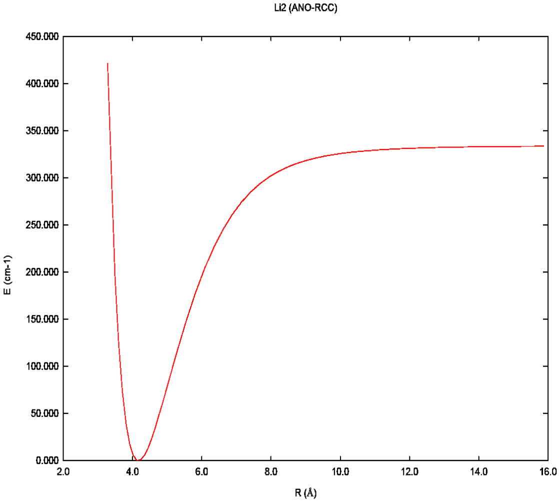
DEA calculations: PECs of Li_2

$1^3\Sigma_u^+$ state – comparison with experiment



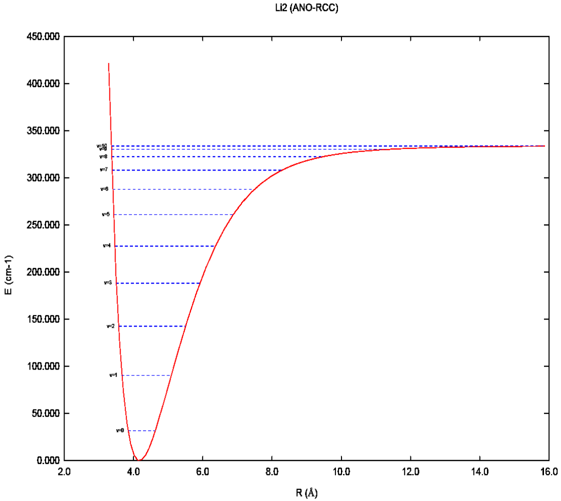
DEA calculations: $1^3\Sigma_u^+$ of Li$_2$

potential energy curve



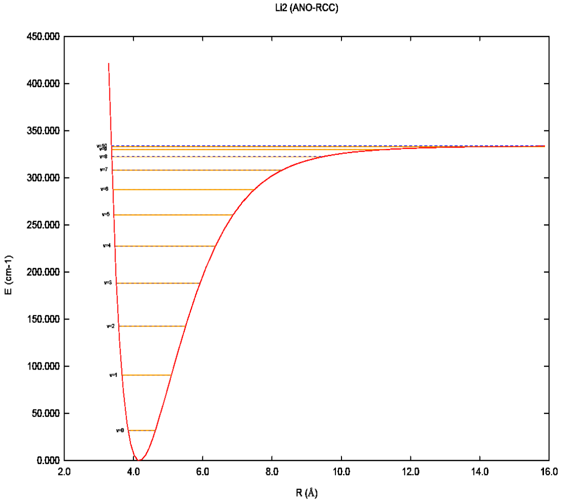
DEA calculations: $1^3\Sigma_u^+$ of Li_2

Vibrational levels - R. J. Le Roy LEVEL 8.0 package



DEA calculations: $1^3\Sigma_u^+$ of Li_2

Vibrational levels - comparison with experiment



$1^3\Sigma_u^+$: vibrational levels - comparison with experiment

	E_v (cm^{-1})		
v	IH-FS-CCSD (2,0)	Δ	EXP[a)]
0	31.6	-0.3	31.9
1	90.3	-0.2	90.5
2	142.3	-0.2	142.5
3	188.2	0.0	188.2
4	227.7	0.0	227.7
5	260.9	0.1	260.8
6	287.8	0.1	287.7
7	308.3	0.2	308.1
8	322.3	0.1	322.2
9	330.3	0.1	330.2
10	333.6	0.3	333.3
MAD		**0.15**	

[a)] C.Linton, et al., *J. Mol. Spec.*, **196**, 20 (1999).

$1^3\Sigma_u^+$: comparison with experiment and other theoretical works

	E_v (cm^{-1})				
v	IH-FS-CCSD (2,0)	Δ	EXP	QCISDT$^{a)}$	$\Delta^{a)}$
0	31.6	-0.3	31.9	32.2	0.3
1	90.3	-0.2	90.5	91.2	0.7
2	142.3	-0.2	142.5	143.6	1.1
3	188.2	0.0	188.2	189.6	1.4
4	227.7	0.0	227.7	229.4	1.7
5	260.9	0.1	260.8	262.8	2.0
6	287.8	0.1	287.7	289.7	2.0
7	308.3	0.2	308.1	310.0	1.9
8	322.3	0.1	322.2	323.7	1.5
9	330.3	0.1	330.2	331.1	0.9
10	333.6	0.3	333.3	333.8	0.5
MAD		**0.15**			**1.27**

$^{a)}$ M. D. Halls, et al., *Chem. Phys. Lett.*, **339**, 427 (2001).

$1^3\Sigma_u^+$: comparison with experiment and other theoretical works

	E_v (cm^{-1})				
v	IH-FS-CCSD (2,0)	Δ	EXP	SAC-CI$^{a)}$	$\Delta^{a)}$
0	31.6	-0.3	31.9	32.4	0.5
1	90.3	-0.2	90.5	92.2	1.7
2	142.3	-0.2	142.5	145.3	2.8
3	188.2	0.0	188.2	192.0	3.8
4	227.7	0.0	227.7	231.3	3.6
5	260.9	0.1	260.8	265.2	4.4
6	287.8	0.1	287.7	291.6	3.9
7	308.3	0.2	308.1	312.4	4.3
8	322.3	0.1	322.2	326.1	3.9
9	330.3	0.1	330.2	333.8	3.6
10	333.6	0.3	333.3	337.7	4.4
MAD		**0.15**			**3.35**

$^{a)}$ D.-H. Shi, et al., *Chin. Phys. Soc.*, **16**, 2701 (2007).

$1^3\Sigma_u^+$: comparison with experiment and other theoretical works

	E_v (cm^{-1})				
v	IH-FS-CCSD (2,0)	Δ	EXP	Eff.pot.$^{a)}$	$\Delta^{a)}$
0	31.6	-0.3	31.9	31	-0.9
1	90.3	-0.2	90.5	89	-1.5
2	142.3	-0.2	142.5	140	-2.5
3	188.2	0.0	188.2	184	-4.2
4	227.7	0.0	227.7	223	-4.7
5	260.9	0.1	260.8	255	-5.8
6	287.8	0.1	287.7	281	-6.7
7	308.3	0.2	308.1	300	-8.1
8	322.3	0.1	322.2	313	-9.2
9	330.3	0.1	330.2	-	-
10	333.6	0.3	333.3	-	-
MAD		**0.15**			**4.84**

$^{a)}$ I. Schmidt-Mink et al., *Chem. Phys.*, **92**, 263 (1985).

$1^3\Sigma_u^+$: comparison with experiment and other theoretical works

	E_v (cm^{-1})				
v	IH-FS-CCSD (2,0)	Δ	EXP	Eff.pot.$^{a)}$	$\Delta^{a)}$
0	31.6	-0.3	31.9	32.4	0.5
1	90.3	-0.2	90.5	92.4	2.0
2	142.3	-0.2	142.5	145.9	3.4
3	188.2	0.0	188.2	193.0	4.8
4	227.7	0.0	227.7	233.7	6.0
5	260.9	0.1	260.8	268.0	7.2
6	287.8	0.1	287.7	295.7	8.0
7	308.3	0.2	308.1	317.1	9.0
8	322.3	0.1	322.2	331.6	9.4
9	330.3	0.1	330.2	339.8	9.6
10	333.6	0.3	333.3	343.5	10.2
MAD		**0.15**			**6.37**

$^{a)}$ P. Jasik et al., *Chem. Phys.*, **323**, 563 (2006).

DEA calculations: Li_2 $1^3\Sigma_u^+$ state

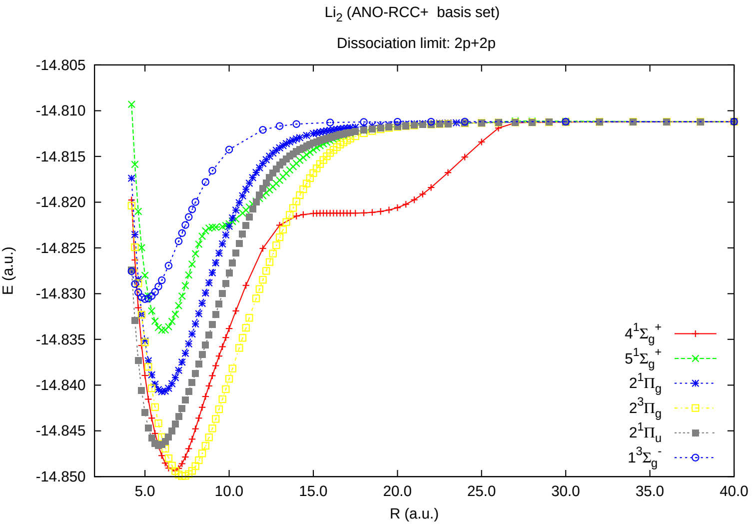
Spectroscopic constants

	R_e (Å)	D_e (cm^{-1})	ω_e (cm^{-1})	T_e (eV)
FS-CCSD (2,0)	4.169	334	65	1.008
exp.$^{a)}$	4.171	333	65	1.014
exp.$^{b)}$	4.170	334	-	-

$^{a)}$ X. Xie et al., *J. Chem. Phys.*, **83**, 6193 (1985);
C. Linton et al., *J. Chem. Phys*, **91**, 6036 (1989).
$^{b)}$ N. S. Dattani et al., *J. Mol. Spect.* **268**, 199 (2011).

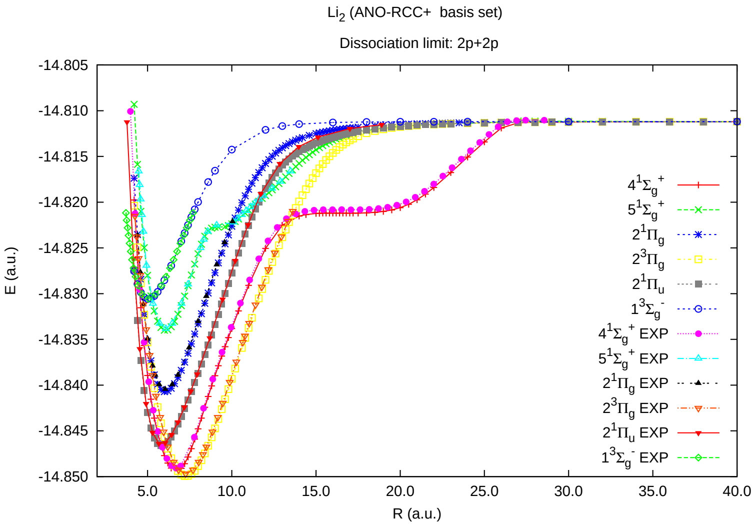
DEA calculations: PECs of Li_2

Dissociation limit: 2P+2P



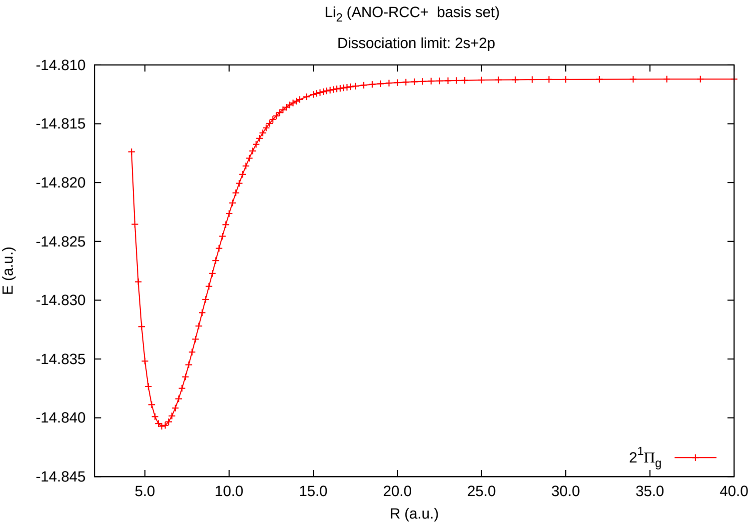
DEA calculations: PECs of Li_2

Dissociation limit: 2P+2P – comparison with experiment



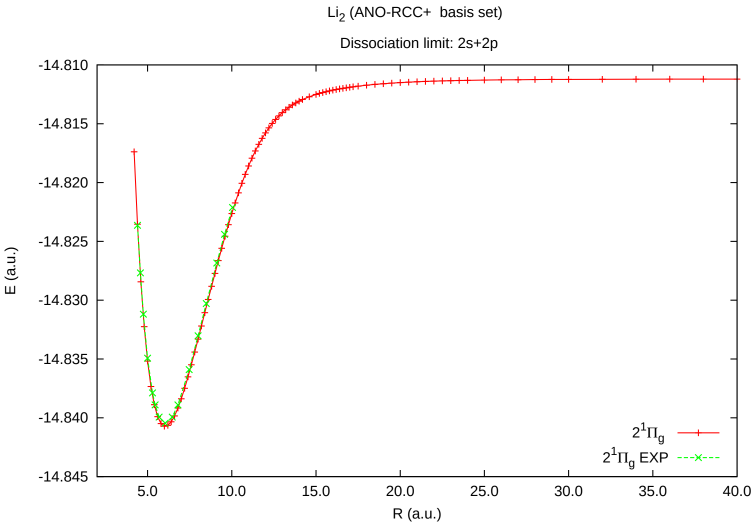
DEA calculations: PECs of Li_2

$2^1\Pi_g$ state



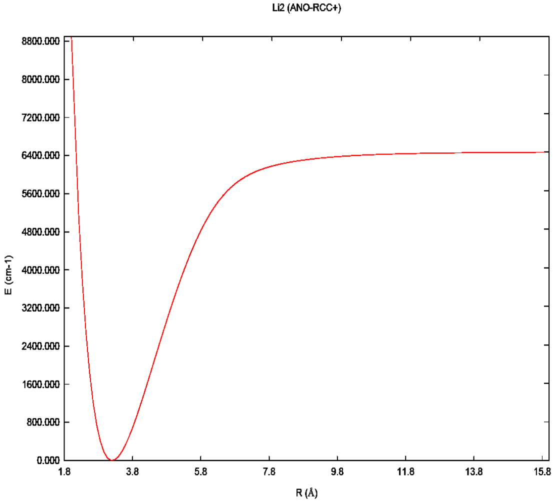
DEA calculations: PECs of Li_2

$2^1\Pi_g$ state – comparison with experiment



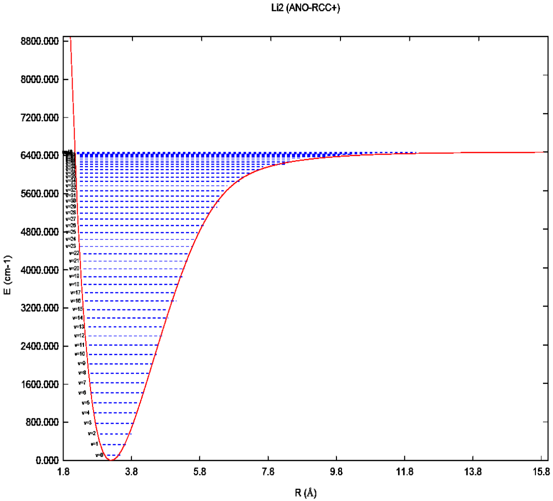
DEA calculations: $2^1\Pi_g$ of Li_2

potential energy curve



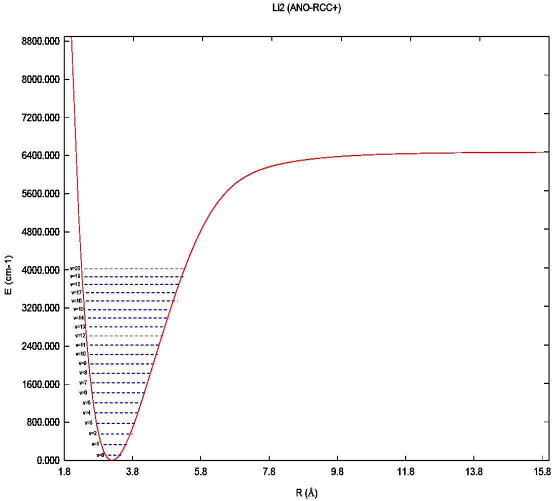
DEA calculations: $2^1\Pi_g$ of Li$_2$

Vibrational levels



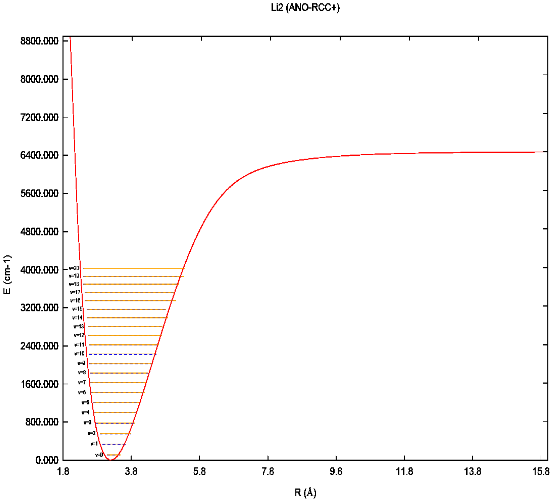
DEA calculations: $2^1\Pi_g$ of Li_2

Vibrational levels



DEA calculations: $2^1\Pi_g$ of Li$_2$

Vibrational levels - comparison with experiment



$2^1\Pi_g$: vibrational levels - comparison with experiment

	E_v (cm^{-1})		
v	IH-FS-CCSD (2,0)	Δ	EXP[a)]
0	112.3	-1.9	114.2
1	338.4	-1.9	340.3
2	561.4	-1.7	563.1
3	781.0	-1.7	782.7
4	997.4	-1.7	999.1
5	1210.7	-1.7	1212.4
6	1420.7	-1.8	1422.5
7	1627.6	-1.8	1629.4
8	1831.3	-1.9	1833.2
9	2031.8	-2.0	2033.8
10	2229.2	-1.9	2231.1

a) R.A. Bernheim, et al., *J. Chem. Phys.*, **74**, 749 (1981).

$2^1\Pi_g$: vibrational levels - comparison with experiment

	E_v (cm^{-1})		
v	IH-FS-CCSD (2,0)	Δ	EXP$^{a)}$
11	2423.3	-2.0	2425.3
12	2614.3	-2.0	2616.3
13	2802.0	-2.0	2804.0
14	2986.5	-1.9	2988.4
15	3167.8	-1.7	3169.5
16	3345.7	-1.5	3347.2
17	3520.2	-1.4	3521.6
18	3691.3	-1.1	3692.4
19	3859.0	-0.8	3859.8
20	4023.1	-0.6	4023.7
...	...	...	...
49	6469.7	-	-
MAD		**1.66**	

$^{a)}$ R.A. Bernheim, et al., *J. Chem. Phys.*, **74**, 749 (1981).

$2^1\Pi_g$: comparison with experiment and other theoretical works

Vibrational energy levels $\mathbf{E_v}$ $\mathbf{(cm^{-1})}$

	MAD
FS-CCSD (2,0)$^{a)}$	1.66
SAC-CI$^{b)}$	58.02
Eff.pot.$^{c)}$	9.79

$^{a)}$ This work; $^{b)}$ D.-H. Shi, et al., *Commun Theor. Phys.*, **47**, 1114 (2007); $^{c)}$ P. Jasik, et al., *Chem. Phys.*, **323**, 563 (2006)

DEA calculations: Li_2 $2^1\Pi_g$ state

Spectroscopic constants

	R_e (Å)	D_e (cm^{-1})	ω_e (cm^{-1})	T_e (eV)
FS-CCSD (2,0)	3.201	6481	230	3.944
exp.$^{a)}$	3.201	6455	230	3.951

$^{a)}$ R. A. Bernheim et al., *J. Chem. Phys.*, **74**, 2749 (1981)

DEA calculations: Li_2

Spectroscopic constants: dissociation limit 2S+2P

states: $2^1\Sigma_g^+$, $1^3\Sigma_g^+$, $1^1\Sigma_u^+$, $2^3\Sigma_u^+$, $1^1\Pi_g$, $1^3\Pi_g$, $1^1\Pi_u$, $1^3\Pi_u$

	R_e(Å)	$D_e(cm^{-1})$	$\omega_e(cm^{-1})$	$T_e(eV)$
$\mathbf{MAE}_{present\ work}$ [a)]	**0.004**	**21**	**1**	**0.003**
$\mathbf{MAE}_{JS}$ [b)]	**0.010**	**79**	**1**	**0.007**
$\mathbf{MAE}_{PS}$ [c)]	**0.010**	**107**	**2**	**0.015**

[a)] **M. Musial, S. A. Kucharski,** *J. Chem. Theory Comput.*, **10, 1200 (2014).**

[b)] **JS: P. Jasik, J. Sienkiewicz,***J. E. Chem. Phys.*, **323, 563 (2006).**

[c)] **PS: R. Poteau, F. Spiegelmann,** *J. Mol. Spectrosc.*, **171, 299 (1995).**

DEA calculations: Li_2

Spectroscopic constants: dissociation limit 2S+3S

states: $3^1\Sigma_g^+$, $2^3\Sigma_g^+$, $2^1\Sigma_u^+$, $3^3\Sigma_u^+$

	$R_e(\mathbf{Å})$	$D_e(cm^{-1})$	$\omega_e(cm^{-1})$	$T_e(eV)$
$\mathbf{MAE}_{present\ \ work}{}^{a)}$	**0.015**	**33**	**1**	**0.009**
$\mathbf{MAE}_{JS}{}^{b)}$	**0.016**	**57**	**1**	**0.006**
$\mathbf{MAE}_{PS}{}^{c)}$	**0.017**	**67**	**2**	**0.009**

a) **M. Musial, S. A. Kucharski,** *J. Chem. Theory Comput.,* **10, 1200 (2014).**

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c) **PS: R. Poteau, F. Spiegelmann,** *J. Mol. Spectrosc.,* **171, 299 (1995).**

DEA calculations: Li_2

Spectroscopic constants: dissociation limit 2P+2P

states: $4^1\Sigma_g^+$, $4^3\Sigma_u^+$, $5^3\Sigma_u^+$, $5^1\Sigma_g^+$, $2^1\Pi_g$, $2^3\Pi_g$, $2^1\Pi_u$, $2^3\Pi_u$, $1^1\Delta_g$, $1^3\Delta_u$, $1^1\Sigma_u^-$, $1^3\Sigma_g^-$

	$R_e(\text{Å})$	$D_e(cm^{-1})$	$\omega_e(cm^{-1})$	$T_e(eV)$
$\mathbf{MAE}_{present\ work}$ $^{a)}$	**0.024**	**18**	**2**	**0.009**
$\mathbf{MAE}_{JS}$ $^{b)}$	**0.030**	**174**	**2**	**0.006**
$\mathbf{MAE}_{PS}$ $^{c)}$	**0.059**	**96**	**3**	**0.009**

$^{a)}$ **M. Musial, S. A. Kucharski,** *J. Chem. Theory Comput.*, **10, 1200 (2014).**

DEA calculations: Na$_2$

Na$_2$ molecule

- Basis set: uncontracted ANO-RCC with additional two diffuse functions for s, p, d shells (248 basis functions)
- model space: 7396 configurations

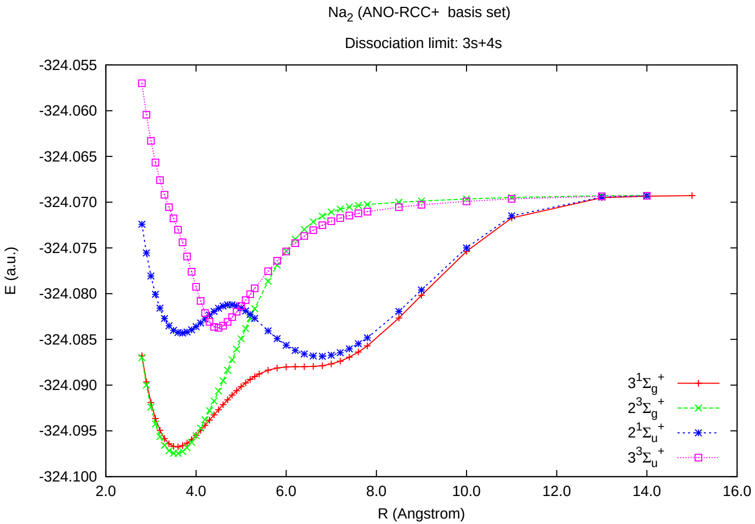
DEA calculations: Na_2

Potential energy curves for 34 electronic states dissociating into the following asymptotic limits:

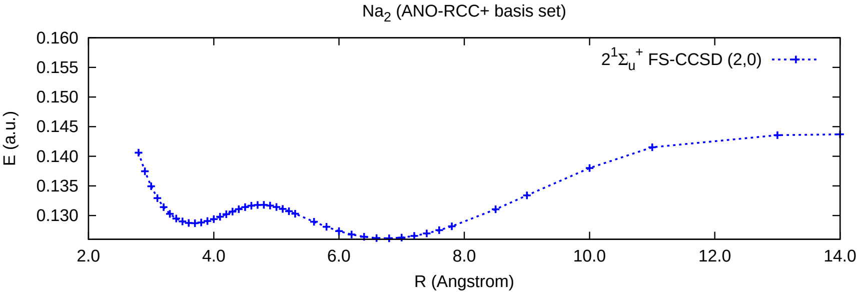
3s+2s	2 states	(2)
3s+2p	8 states	(12)
3s+4s	4 states	(4)
3s+3d	12 states	(20)
3s+4p	8 states	(12)

DEA calculations: Na_2

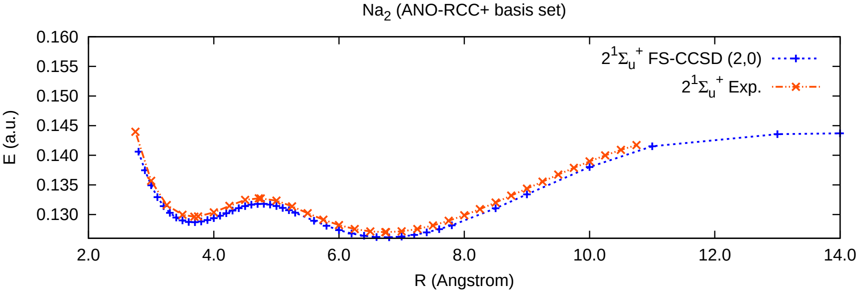
Dissociation limit: 3S+4S



DEA calculations: Na_2 double minimum $2^1\Sigma_u^+$ state



DEA calculations: Na_2 double minimum $2^1\Sigma_u^+$ state from



DEA calculations: Na$_2$ double minimum $2^1\Sigma_u^+$ state

Spectroscopic constants

	R_e (Å)	D_e (cm^{-1})	ω_e (cm^{-1})	T_e (eV)
inner well	3.676	3317	106	3.502
exp.	3.688	3304	106	3.528
outer well	6.750	3878	52	3.432
exp.	6.736	3880	53	3.457

DEA calculations: NaLi

NaLi molecule

- Basis set: same as before (238 basis functions)
- model space: 4489

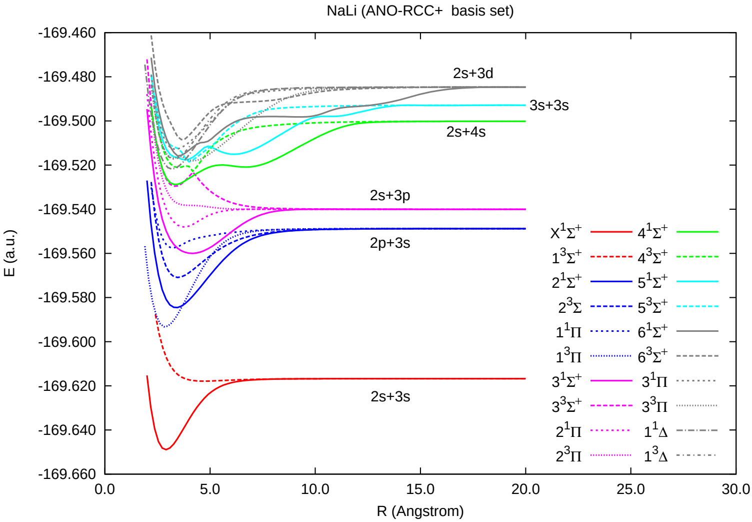
DEA calculations: NaLi

Potential energy curves for 20 electronic states dissociating into the following asymptotic limits:

2s+2s	2 states	(2)
3p+3s	4 states	(6)
3s+3p	4 states	(6)
2s+4s	2 states	(2)
3s+3s	2 states	(2)
2s+3d	6 states	(10)

DEA calculations: NaLi GS and EEs

ANO-RCC+ basis set: 238 basis functions; active space: 68



Multireference Fock space CC method

APPLICATIONS

(1,1) sector

Applications of (1,1) sector

Vertical excitation energies (in eV) for $N_2^{a)}$ as obtained with the FS-CC at the CCSD and CCSDT levels with the aug-cc-pVQZ basis set.

Mol.	Sym.	IH-FS		*Exp.*
		CCSD	CCSDT	
N_2	**$^1\Pi_g$**	**9.325**	**9.333**	*9.340*
(12,4)		**(-0.015)**	**(-0.007)**	
	$^1\Sigma_u^-$	**10.035**	**9.863**	*9.880*
		(0.155)	**(-0.017)**	
	$^1\Delta_u$	**10.518**	**10.270**	*10.270*
		(0.248)	**(0.000)**	
	$^1\Pi_u$	**13.396**	**13.136**	*13.050*
		(0.346)	**(0.086)**	
MAE		**0.191**	**0.028**	

Applications of (1,1) sector

Vertical excitation energies (in eV) for CO$^{a)}$ as obtained with the FS-CC at the CCSD and CCSDT levels with the aug-cc-pVQZ basis set.

Mol.	Sym.	IH-FS		*Exp.*
		CCSD	CCSDT	
CO	$^1\Pi$	8.605	8.482	*8.520*
(12,4)		(0.085)	(-0.038)	
	$^1\Sigma-$	10.167	9.958	*9.900*
		(0.267)	(0.058)	
	$^1\Delta$	10.365	10.091	*10.130*
		(0.235)	(-0.039)	
	$^1\Sigma^+$	11.133	10.923	*10.780*
		(0.353)	(0.143)	
MAE		0.235	0.070	

CONCLUSIONS

- It is well known – for about three decades – that the Fock space coupled cluster approach provides a reliable size-extensive results for excitation energies, ionization potentials and electron affinities.
- The computational problems in reaching efficient solutions within the standard FS formulation significantly slowed down its development.
- The new opening for the wider applications of the FS-CC method is connected with the introduction by Meissner and Bartlett new formalism for the (1,1) sector based on the intermediate Hamiltonian approach.

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CONCLUSIONS - continued

- Applying the same scheme to other sectors made the FS-CC method a robust and accurate tool for high level calculations.
- Particularly attractive scheme is based on the DEA strategy used for the calculations for accurate PECs based on FS (2,0) sector.

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The End

THANK YOU FOR YOUR ATTENTION