

Fock space coupled cluster method based on the RHF reference for the description of the potential energy curves for the alkali metal dimers

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ABSTRACT

The intermediate Hamiltonian (IH) Fock space (FS) Coupled Cluster (CC) scheme for the (2,0) sector, reported recently [1], is introduced to study double electron attached states. The method has a useful feature that when applied to the doubly ionized atoms or molecules (A^{2+}) it provides a characteristics of the neutral systems (A). This approach is particularly advantageous in the studies of the potential energy curves (PECs) for the alkali metal dimers (Me_2). The closed shell Me_2 molecule dissociates into open shell fragments which makes it difficult to generate correct PECs with the closed shell methods. However, the doubly ionized Me_2^{2+} system provides a very convenient reference dissociating into the closed shell fragments (Me^+). Thus when applying the (2,0) FSCC scheme to study the PECs for the Me_2^{2+} ions we obtain a correct description of the alkali metal dimers in the whole range of the interatomic distances. An important feature of the method is its formulation via intermediate Hamiltonian formalism which eliminates the well known deficiencies of the standard FS approach like, e.g. intruder state problem. In the current work we study the potential energy curves for the ground and excited states of the Li_2 , Na_2 and K_2 dimers. In all cases we are able to compute the smooth PECs for the whole range of interatomic distances from equilibrium to the dissociation limit. The other advantage of the approach is its rigorous size-extensivity allowing to reproduce the atomic excitation energies at the infinite interatomic distance.

[1] M. Musiał, "Multireference Fock space coupled cluster method in the effective and intermediate Hamiltonian for the (2,0) sector", *J. Chem. Phys.*, **136**, 134111 (2012).

THEORY

EOM-CC for DEA

$$\tilde{H} = \begin{bmatrix} \langle D | \tilde{H} | D \rangle & \langle D | \tilde{H} | T \rangle \\ \langle T | \tilde{H} | D \rangle & \langle T | \tilde{H} | T \rangle \end{bmatrix}$$

$\tilde{H} = e^{-T} H e^T \rightarrow$ similarity transformed Hamiltonian

DEA: $D \equiv \Phi^{ab}$; $T \equiv \Phi_i^{abc}$

Variants:

- **DEA-EOM-CCSD**
 - GS: $T = T_1 + T_2$ (scaling $n^6(n_o^2 n_v^4)$)
 - DEA part: $R = R_2$ (scaling $n^4(n_o^4)$)
- **DEA-EOM-CCSDT**
 - GS: $T = T_1 + T_2 + T_3$ (scaling $n^8(n_o^2 n_v^6)$)
 - DEA part: $R = R_2 + R_3$ (scaling $n^6(n_o^2 n_v^4)$)
- **DEA-EOM-CCSDT'**
 - GS: $T = T_1 + T_2$ (scaling $n^6(n_o^2 n_v^4)$)
 - DEA part: $R = R_2 + R_3$ (scaling $n^6(n_o^2 n_v^4)$)

IH-FS-CC for DEA

$$H_I = \langle D | \tilde{H} | D \rangle$$

$H_I = \underbrace{\tilde{H}}_H + \underbrace{\text{dressing}}_H \rightarrow$ intermediate Hamiltonian

DEA: $D \equiv \Phi^{ab}$

Variant:

- **IH-FS-CCSD (2,0) sector**
 - 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 $n^5(n_o^2 n_v^3)$)

Hierarchy of the FS solutions for DEA

sector (0,0)
(GS)

sector (1,0)
(EA)

sector (2,0)
(DEA)

Indirect applications of the DEA calculations

Ground and excited states energies from the DEA calculations

To describe the A molecule (e.g., Na_2) we do DEA calculations for the A^{2+} system (Na_2^{2+})

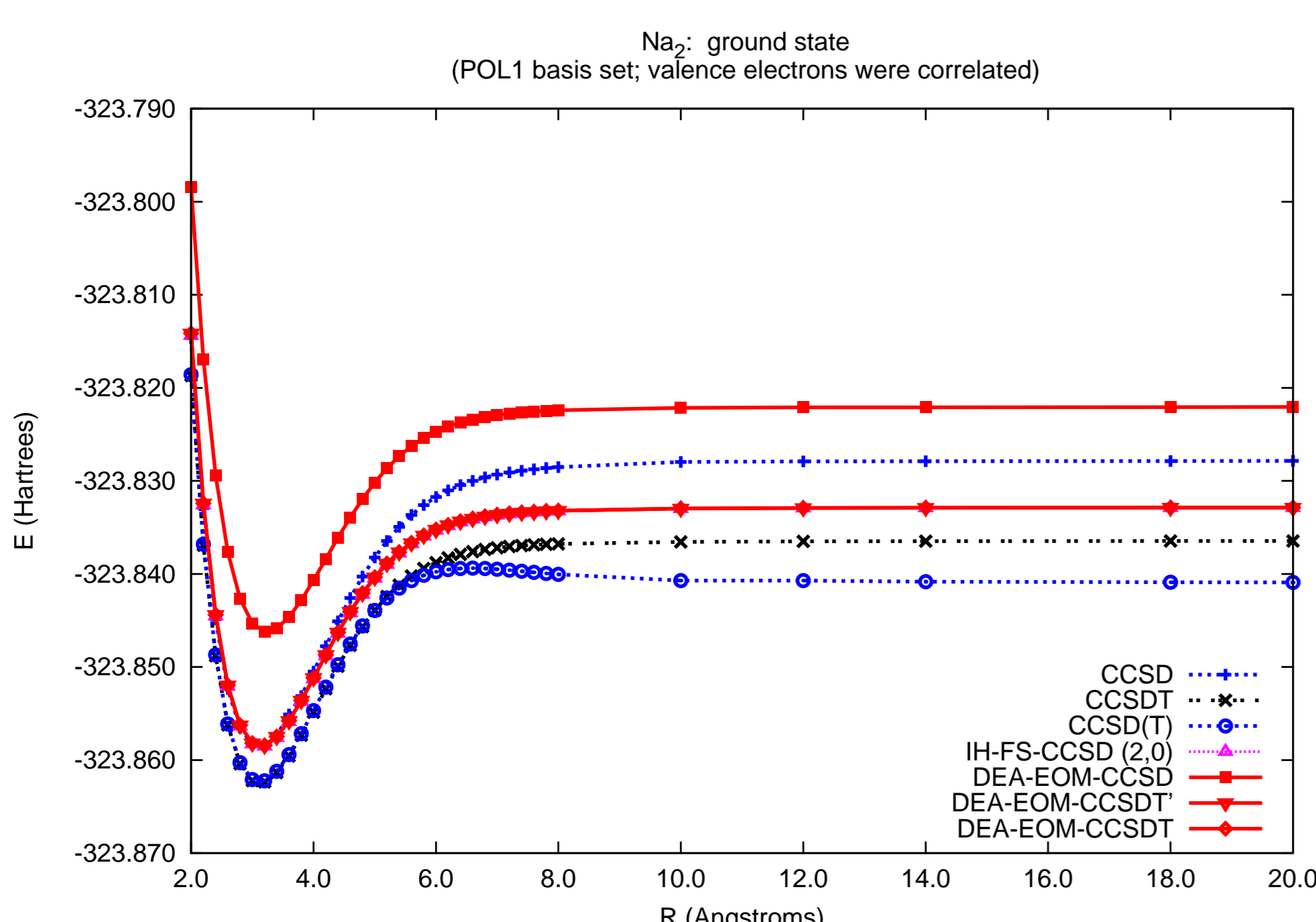
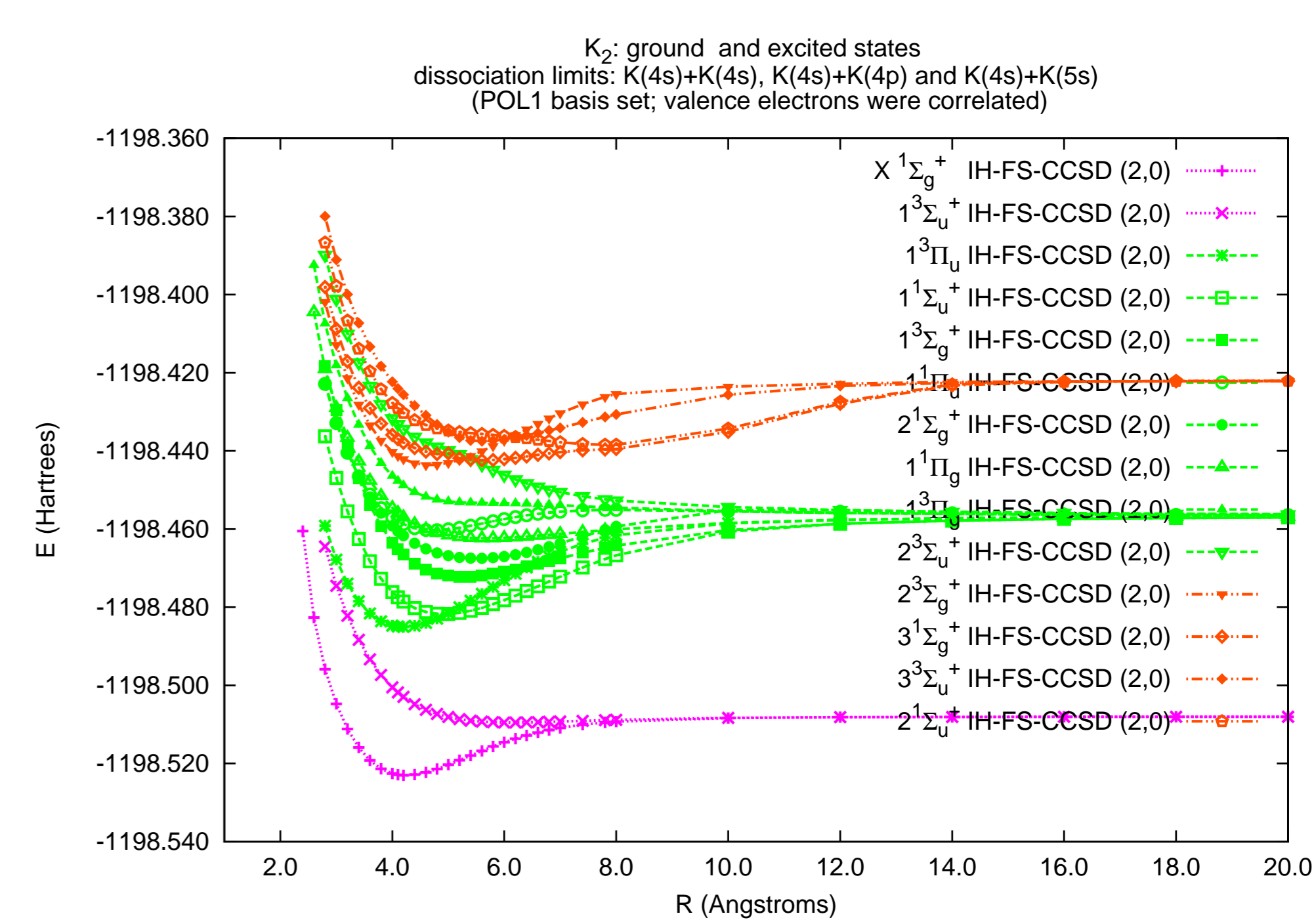
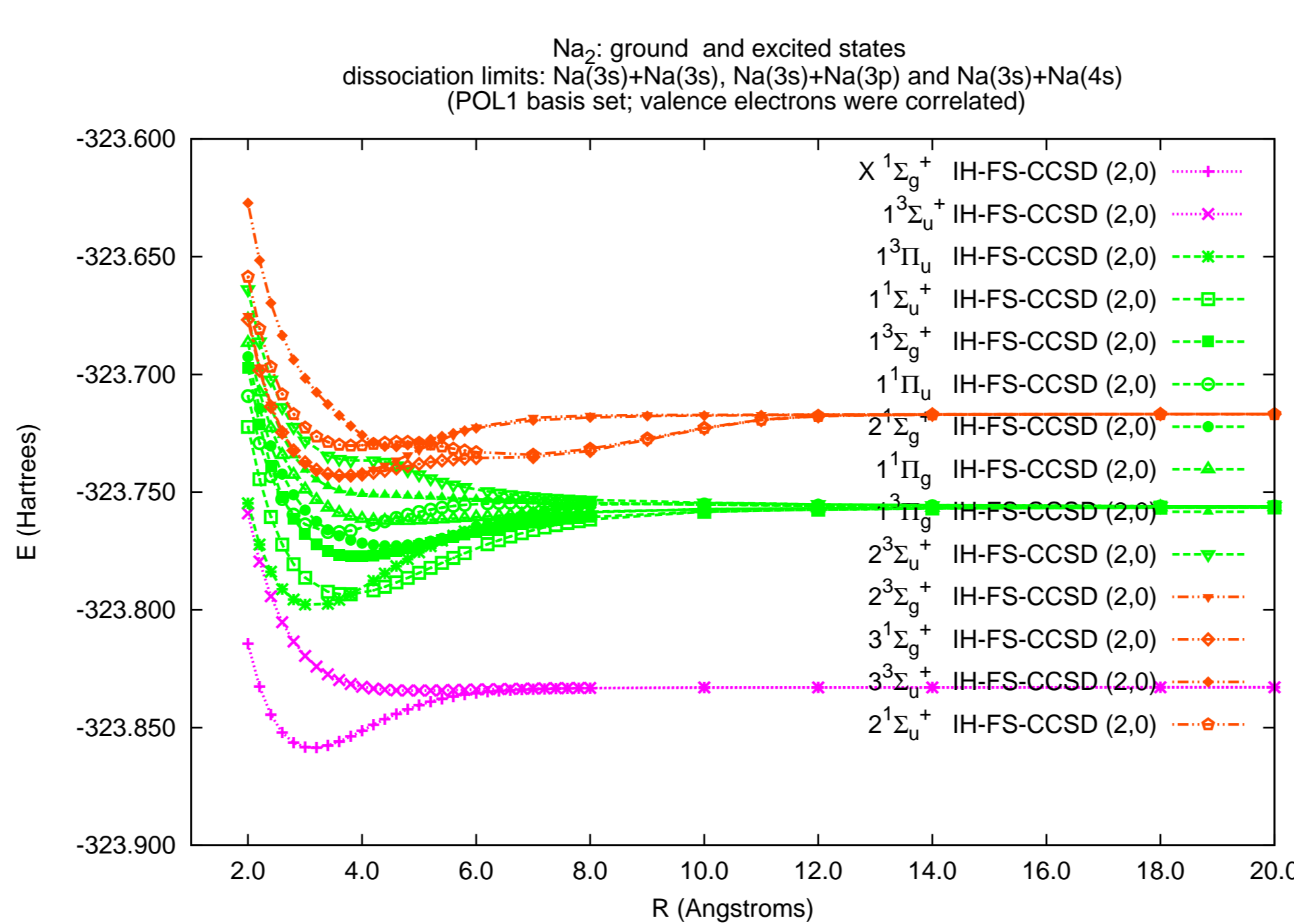
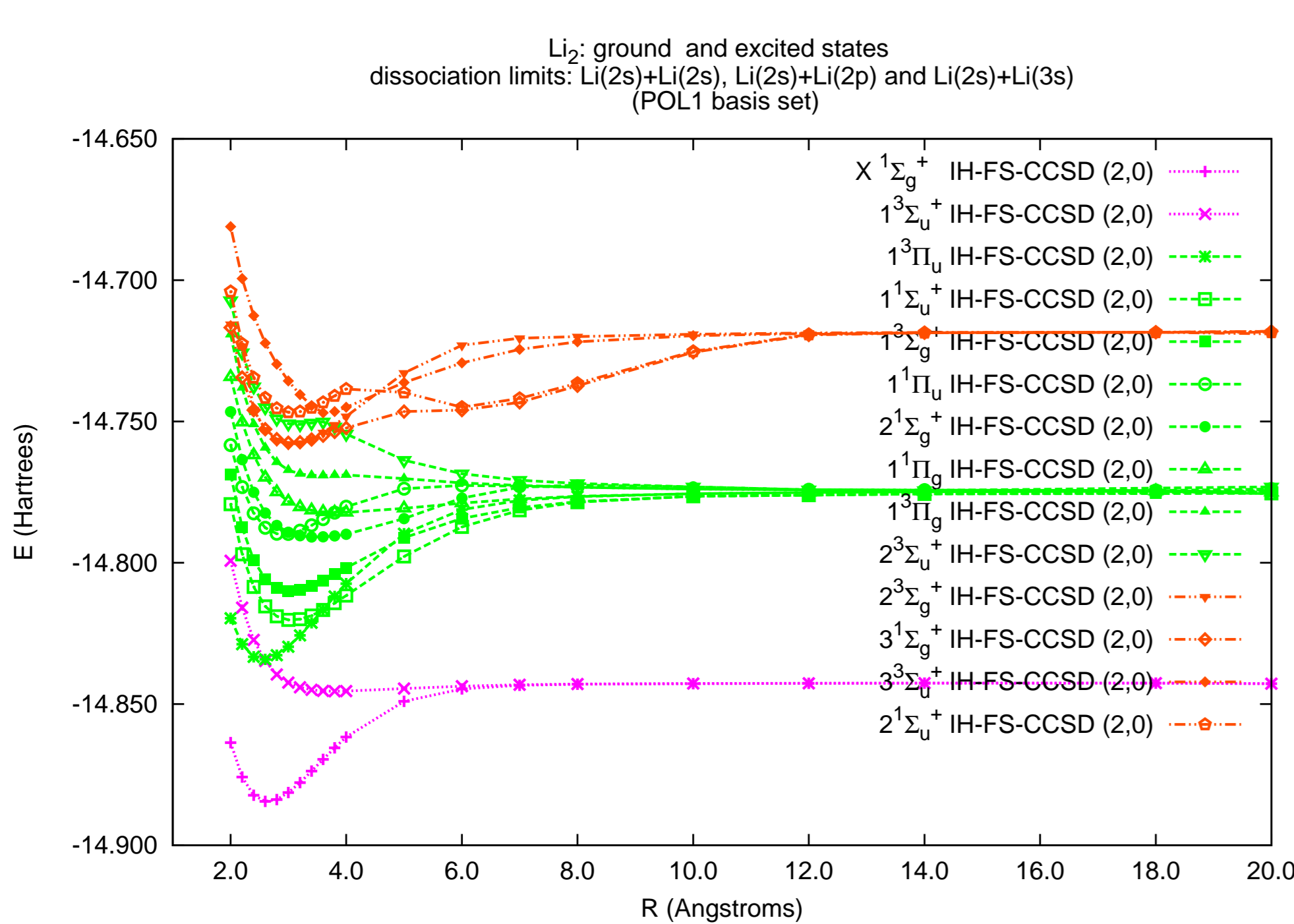
Generally:

$$A^{2+} \xrightarrow{DEA} A$$

For Na_2 :

$$Na_2^{2+} \xrightarrow{DEA} Na_2$$

RESULTS



Na ₂ : separated atoms	
GS energy (au) for Na ₂	
IH-FS-CCSD (2,0) sector	
E_{Na_2}	-323.832888
$2 \times E_{Na}$	-323.832888
Δ	0.000000
GS energy (au) for Na	
EA-EOM-CCSD	
IH-FS-CCSD (1,0)	
E_{Na}	-161.916444

Vertical excitation energies (eV) for Na₂^{a)} in the POL1 basis set.

Sym.	IH-FS-CCSD (2,0)		EE-EOM-CCSD	Exp.
	RHF	UHF		
	Na(3s)+Na(3s)			
1 ³ Σ _u ⁺	1.01	1.00	0.73	
	Na(3s)+Na(3p)			
1 ³ Π _u	1.64	1.63	1.68	
1 ¹ Σ _u ⁺	1.92	1.93	1.82	
1 ³ Σ _g ⁺	2.42	2.40	-	
1 ¹ Π _u	2.55	2.52	2.52	
2 ¹ Σ _g ⁺	2.69	2.74	2.40	
1 ¹ Π _g	2.93	2.96	2.70	
1 ³ Π _g	3.16	3.12	-	
2 ³ Σ _u ⁺	3.50	3.46	-	
	Na(3s)+Na(4s)			
2 ³ Σ _g ⁺	3.25	3.22	-	
3 ¹ Σ _g ⁺	3.26	3.27	3.18	
2 ¹ Σ _u ⁺	3.65	3.59	3.53	
3 ³ Σ _u ⁺	4.20	4.19	-	
MAE	0.15	0.15		

^{a)} Assumed experimental geometry for the GS (R=3.0788 Å).

CONCLUSIONS

- The FS-CC method offers an efficient tool for the evaluation of the DEA.
- Adding (or removing) electron pair helps to preserve the proper spin and space symmetry upon dissociation.
- DEA calculations enable to compute PECs for systems the double cation of which dissociates into closed shell fragments.
- FS-CC approach provides size-extensive results in the DEA calculations.
- An important point is the realization of the FS calculations via efficient IH scheme.

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