New methods to study excited states of atoms and molecules

Monika Musiał

University of Silesia
Institute of Chemistry

Ionized states

IP: ionization potential

$$\mathbf{A} \Longrightarrow \mathbf{A}^+$$

$$\mathbf{IP} = \mathbf{E}_{\mathbf{A}^+} - \mathbf{E}_{\mathbf{A}}$$

DIP: double ionization potential

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

$$\mathbf{DIP} = \mathbf{E}_{\mathbf{A}^{+2}} - \mathbf{E}_{\mathbf{A}}$$

Why ionized states???

Direct application of the IP calculations

Ultraviolet Photoelectron Spectroscopy (UPS)

UPS – measurement of the kinetic energy (E_k) of photoelectrons emitted by ultraviolet photons to determine molecular energy levels in the valence region

$$\mathbf{E}_k = \mathbf{h}\nu - \mathbf{IP}$$

X-ray Photoelectron Spectroscopy (XPS)

XPS - measurement of the kinetic energy of the electrons ejected from the K or L shells by the high energy photon from X-ray region

$$\mathbf{E}_k = \mathbf{h}\nu_x - \mathbf{IP}_{core}$$

Indirect application of the IP calculations

Excitation energies (EE) from the IP calculations

To obtain EEs for the system A with unpaired electron (radical) we calculate IP for the electron attached A^- closed shell system.

- Example: calculation of EEs for the F atom

$\vdots$

$\mathbf{B}$ __

$\mathbf{A}$ __ $\quad |\Delta \mathbf{E}_{\mathrm{A}}\ |\ \Delta \mathbf{E}_{\mathrm{B}}$

$\mathbf{X}$ __

$\mathbf{F}^{\bullet}$

difficult

open shell EE solutions

$\Delta \mathbf{E}_{\mathrm{A}} = \Delta \mathbf{E}_{\mathrm{A}}$

$\vdots$

$\mathbf{B}^{+}$ __

$\mathbf{A}^{+}$ __ $\quad |\Delta \mathbf{E}_{\mathrm{A}}\ |\ \Delta \mathbf{E}_{\mathrm{B}}$

$\mathbf{X}^{+}$ __

$\mathbf{F}^{-}$

straightforward

closed shell IP solutions

Direct application of the DIP calculations

Auger Electron Spectroscopy (AES)

Quantity measured in AES:

ΔE_{Auger} – kinetic energy of the Auger electron

$$\Delta E_{\text{Auger}} = IP_{core} - DIP$$

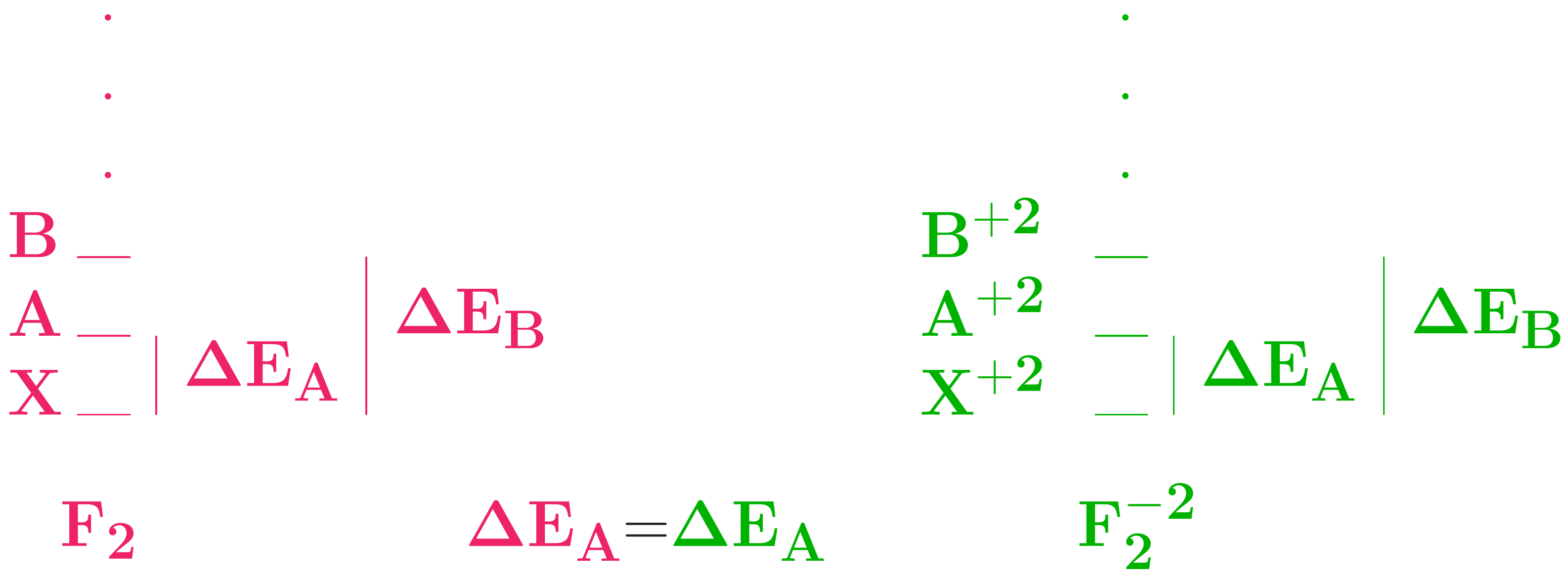
where IP_{core} - core ionization potential

Indirect application of the DIP calculations

Excitation energies from the DIP calculations

To obtain EEs for the A molecule we do DIP calculations for the A^{-2} system.

• Example: calculation of EEs for the F_2 molecule



$\vdots$

B

A

X

ΔE_A

ΔE_B

$\mathbf{F_2}$

$\vdots$

$\mathbf{B^{+2}}$

$\mathbf{A^{+2}}$

$\mathbf{X^{+2}}$

ΔE_A

ΔE_B

$\mathbf{F_2^{-2}}$

$$\Delta E_A = \Delta E_A$$

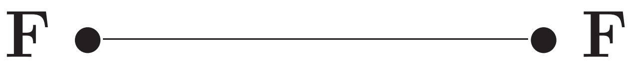
EE solutions

DIP solutions

Equilibrium geometry

- Neutral molecule

F_2



No problem with GS + EE calculations for the equilibrium geometry.

- Double electron attached molecule

F_2^{-2}

No problem with doing DIP calculations for the F_2^{-2} system.

F_2 with separated atoms

- Neutral molecule

$$F_2$$

Reference state is not well defined.

- Double electron attached molecule

$$F_2^{-2}$$

F_2^{-2} system separates into two closed shell sub-units. Very convenient reference function.

The essence of this trick

We do GS calculations for the F_2^{-2} system (with two attached electrons) in order to, in next stage, run DIP calculations.

WHY: because GS for F_2^{-2} is much easier to obtain (for large R).

DIP calculations in the Potential Energy Curves (PEC) production

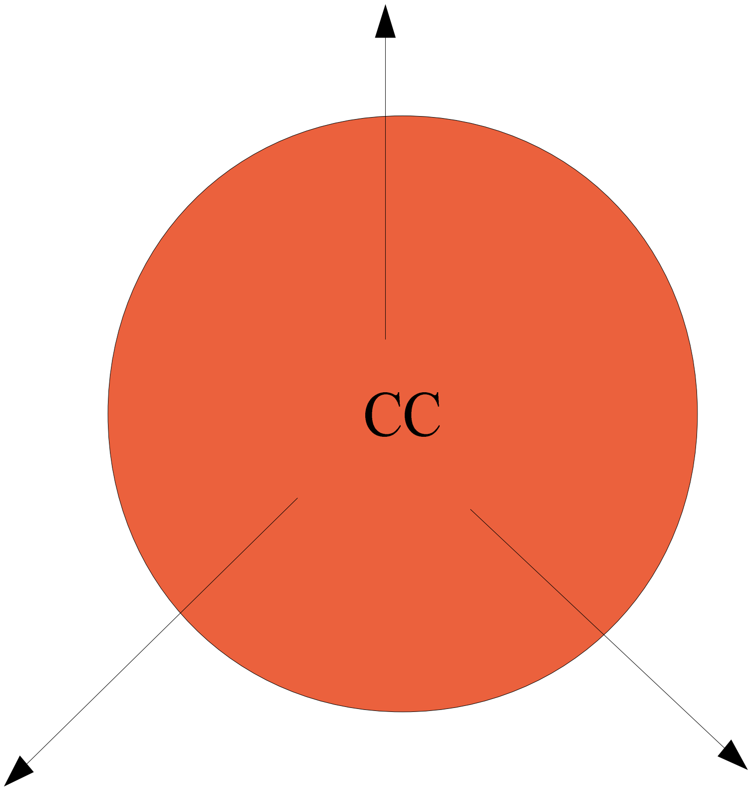
Coupled cluster theory in the study of the ionized states:

- Equation-Of-Motion (EOM) technique
- Fock space (FS) CC approach (or Valence Universal)

IONIZED STATES

- IP-EOM-CC approach
- FS-CC (0,1) sector

- DIP-EOM-CC approach
- FS-CC (0,2) sector



CC

GS

CCSD

CCSDT

IP

IP-EOM-CCSD

FS-CCSD (0,1)

IP-EOM-CCSDT

FS-CCSDT (0,1)

DIP

DIP-EOM-CCSD

FS-CCSD (0,2)

DIP-EOM-CCSDT

FS-CCSDT (0,2)

Rank of the computational procedure in the EOM-CC calculations

GS

CCSD: $\mathbf{n^6}$ $(n_o^2 n_v^4)$

CCSDT: $\mathbf{n^8}$ $\left(n_o^3 n_v^5\right)$

IP-EOM

CCSD: $\mathbf{n^5}$ $(n_o^3 n_v^2)$

CCSDT: $\mathbf{n^7}$ $\left(n_o^3 n_v^4\right)$

DIP-EOM

CCSD: $\mathbf{n^4}$ (n_o^4)

CCSDT: $\mathbf{n^6}$ $\left(n_o^4 n_v^2\right)$

Ionization potential calculations

Comparison with FCI values

Vertical ionization potentials (in eV) related to the FCI values.

Mol.	**Sym.**	**EOM-CCSD**	**EOM-CCSDT**	*FCI*
C_2	$^2\Pi_u$	**0.531**	**0.003**	*12.131*
	$^2\Sigma_u^-$	**0.459**	**0.082**	*14.721*
BH	$3^2\Sigma$	**0.035**	**0.001**	*9.383*
	$2^2\Sigma$	**0.337**	**0.025**	*16.643*
H_2O	$^2B_1$	**-0.173**	**-0.030**	*11.840*
	$^2A_1$	**-0.159**	**-0.023**	*13.850*
	$^2B_2$	**-0.076**	**-0.009**	*18.600*
m.a.e		**0.253**	**0.025**	

Comparison with experimental data

Vertical IPs (in eV) of CO, F_2 and C_2 molecules$^{a)}$ with IP-EOM-CC methods.

Mol.	Sym.	aug-cc-pVQZ CCSD	aug-cc-pVQZ CCSDT	*Exp.*
CO	5Σ	14.26	14.01	*14.01*
	1Π	17.18	17.09	*16.91*
	4Σ	19.89	19.66	*19.72*
F_2	$1\Pi_g$	15.75	15.79	*15.83*
	$1\Pi_u$	19.09	18.97	*18.80*
	$3\Sigma_g^+$	21.27	21.18	*21.10*
C_2	Π_u	13.05	12.61	*12.15*

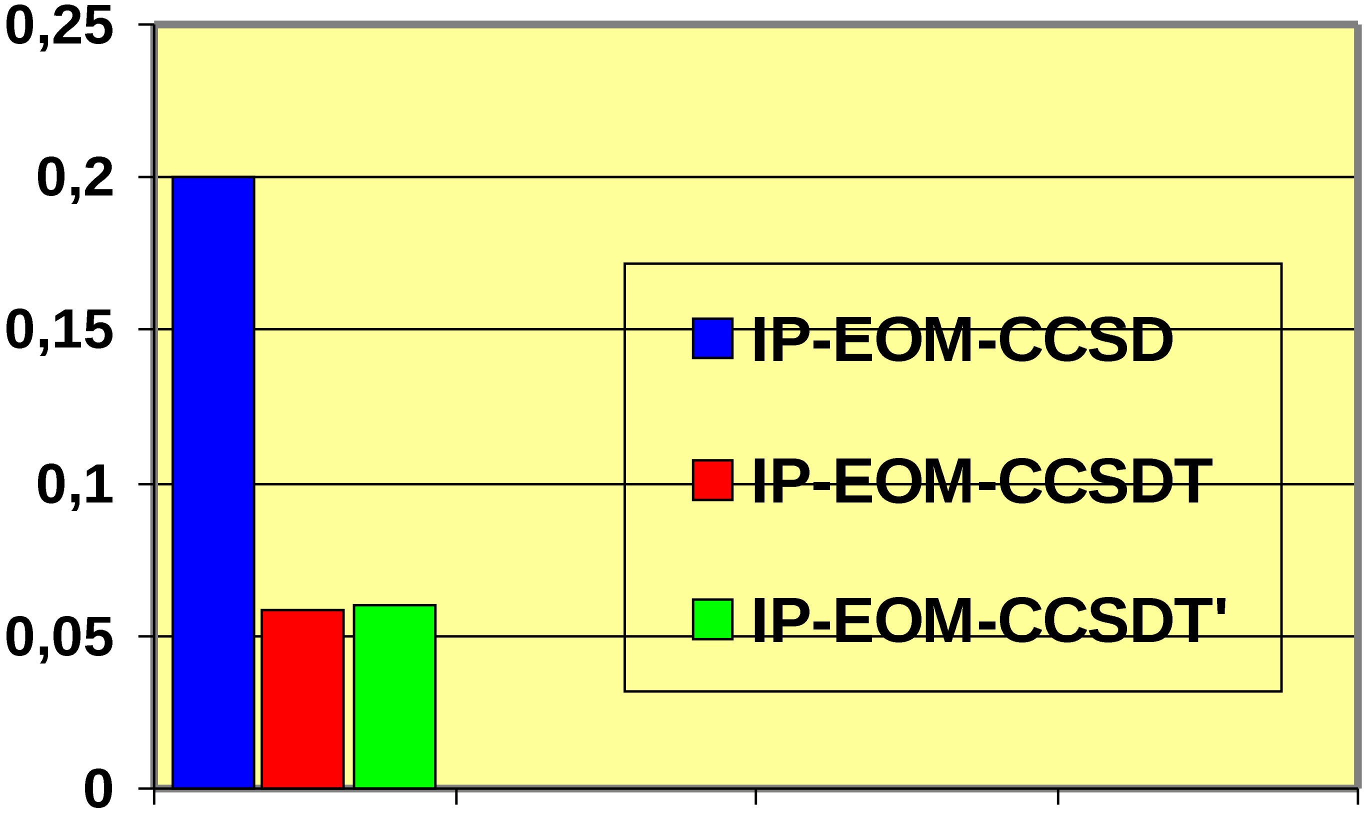
$^{a)}$ CO: R=1.128323 Å, F_2 : R=1.41193 Å, C_2 : R=1.243 Å.

Efficient approximate variant of the IP-EOM-CC method with connected triple excitations

IP-EOM-CCSDT′

GS step	**CCSDT**	n^8	**in full model**
	$\Downarrow$		
GS step	**CCSDT-3**	n^7	**approximate**
IP step	**IP-EOM-CCSDT**	n^7	**rigorous**

Mean absolute deviation (eV) from the experimental data for ionization potentials



Excitation energies for the open shell ionized molecules

Computed excitation energies (in eV) for (open shell) ionized molecules with RHF based IP-EOM-CC methods.

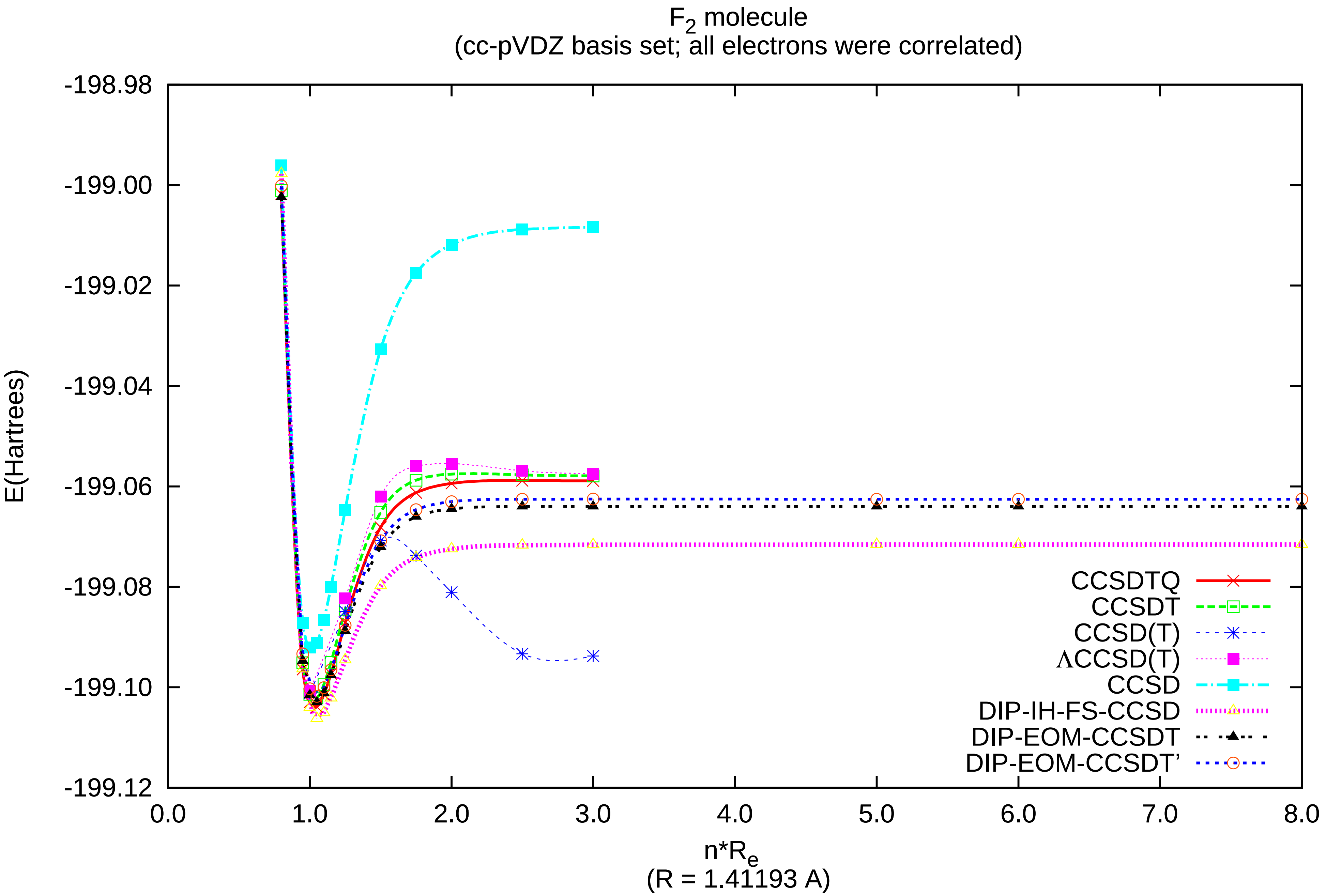
Cation	Nominal state	POL1		aug-cc-pVQZ		*Exp.*
		CCSD	CCSDT	CCSD	CCSDT	
$N_2{}^+$	$^2\Pi_u$	1.68	1.50	1.60	1.45	*1.35*
	$^2\Sigma_u^-$	3.25	3.21	3.27	3.22	*3.17*
CO^+	$^2\Sigma$	5.63	5.71	5.65	5.66	*5.69*
F_2^+	$^2\Sigma_g^+$	5.57	5.42	5.50	5.39	*5.33*

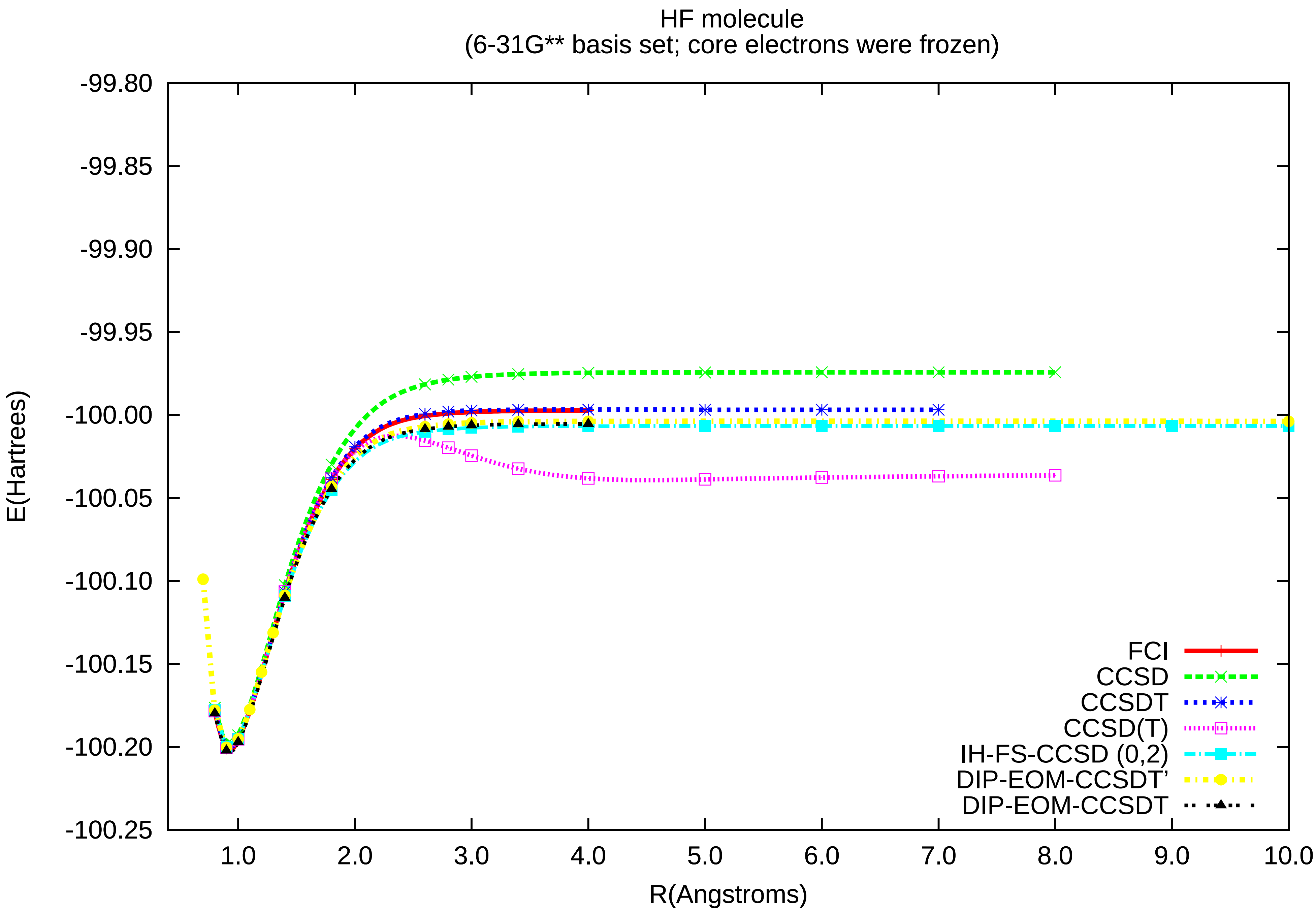
Double ionization potential calculations

Vertical double ionization potentials[a] (in eV) with the EOM-CC and FS-CC methods in the POL1 basis set.

Mol.	Sym.	DIP-EOM			IH-FS (0,2)	*Exp.*
		CCSD	CCSDT	CCSDT'	CCSD	
H_2O	$^3B_1$	49.82	41.34	41.21	40.12	*39.4*
	$^1A_1$	50.39	41.73	41.63	41.75	*41.3*
	$^1B_1$	51.78	43.24	43.14	43.03	*42.0*
	$^3A_2$	53.00	45.39	45.27	44,34	*43.2*
CO	$^1\Sigma^+$	46.72	41.91	41.76	41.82	*41.7*
	$^1\Pi$	47.02	42.71	42.53	42.21	*42.2*
	$^1\Sigma^+$	51.75	45.94	45.72	48.03	*45.8*
C_2H_2	$^1\Delta_g$	38.13	33.88	33.63	33.44	*33.0*
	$^1\Pi_u$	43.71	39.15	38.93	34.30	*37.6*
	$^1\Pi_g$	45.82	41.30	41.09	38.76	*39.3*
C_2H_4	^1A_g	35.59	31.20	30.96	30.95	*30.1*
	^1A_g	37.06	32.79	32.58	32.74	*32.2*
	$^1B_{3u}$	40.66	35.57	35.34	34.73	*34.0*

[a] Assumed experimental geometry for the ground state.


F2 molecule
(cc-pVDZ basis set; all electrons were correlated)
E(Hartrees)
-198.98
-199.00
-199.02
-199.04
-199.06
-199.08
-199.10
-199.12
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
n*Re
(R = 1.41193 A)
CCSDTQ
CCSDT
CCSD(T)
ΛCCSD(T)
CCSD
DIP-IH-FS-CCSD
DIP-EOM-CCSDT
DIP-EOM-CCSDT'


HF molecule
(6-31G** basis set; core electrons were frozen)
-99.80
-99.85
-99.90
-99.95
-100.00
-100.05
-100.10
-100.15
-100.20
-100.25
E(Hartrees)
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
R(Angstroms)
FCI
CCSD
CCSDT
CCSD(T)
IH-FS-CCSD (0,2)
DIP-EOM-CCSDT'
DIP-EOM-CCSDT

Double electron affinity

- DEA: double electron attachment

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

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

- In practice:

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

DEA calculations: $\mathbf{A}$

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

To obtain EEs for the A system we do DEA calculations for the A^{+2} system.

- Neutral molecule

$$Na_2$$

$\dot{\mathbf{N}}\mathbf{a}$ ———- . . . . . . ———- $\dot{\mathbf{N}}\mathbf{a}$

- Double ionized molecule

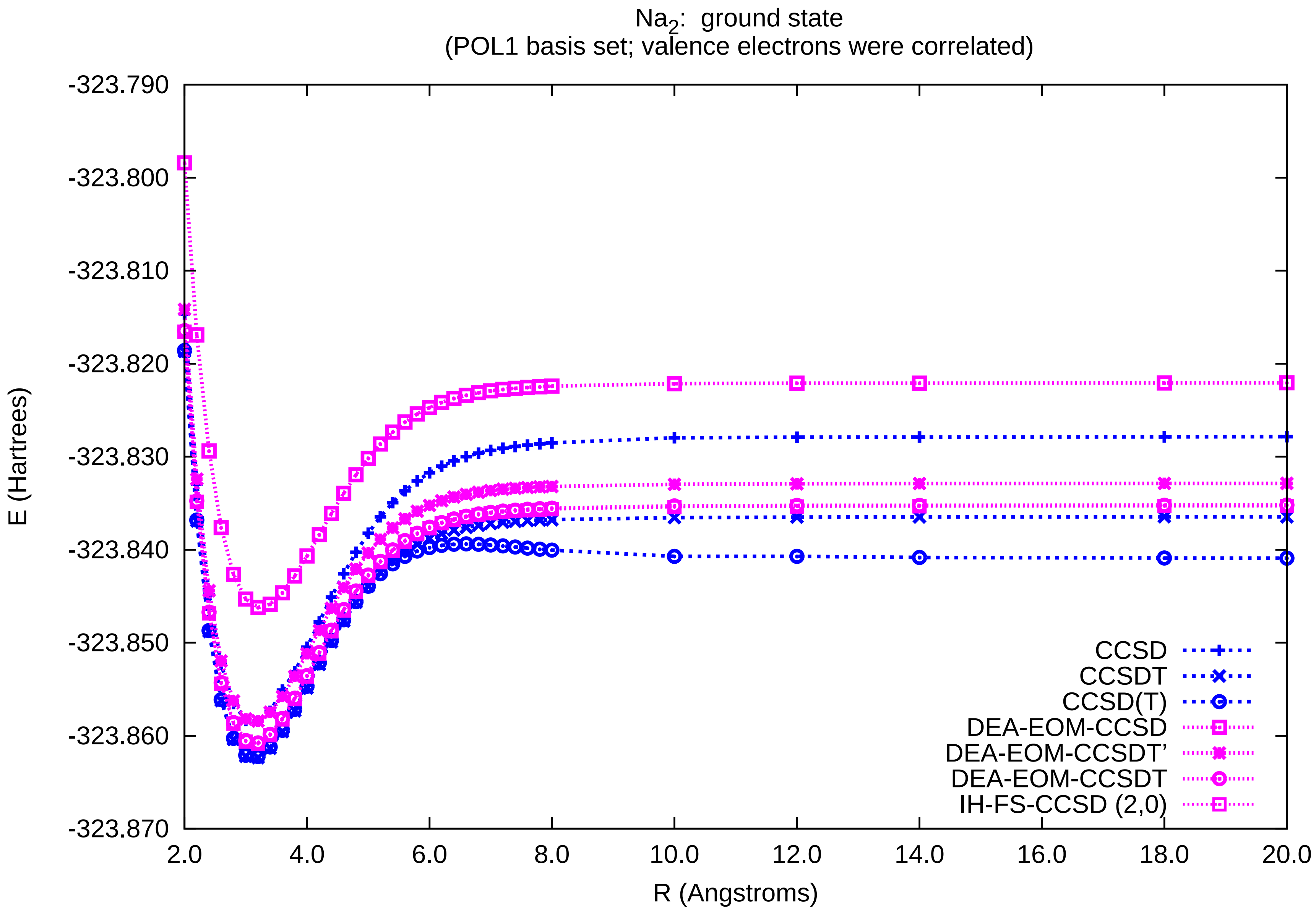
$$Na_2^{+2}$$

$\mathbf{Na}^{+}$ —— . . . . —— $\mathbf{Na}^{+}$

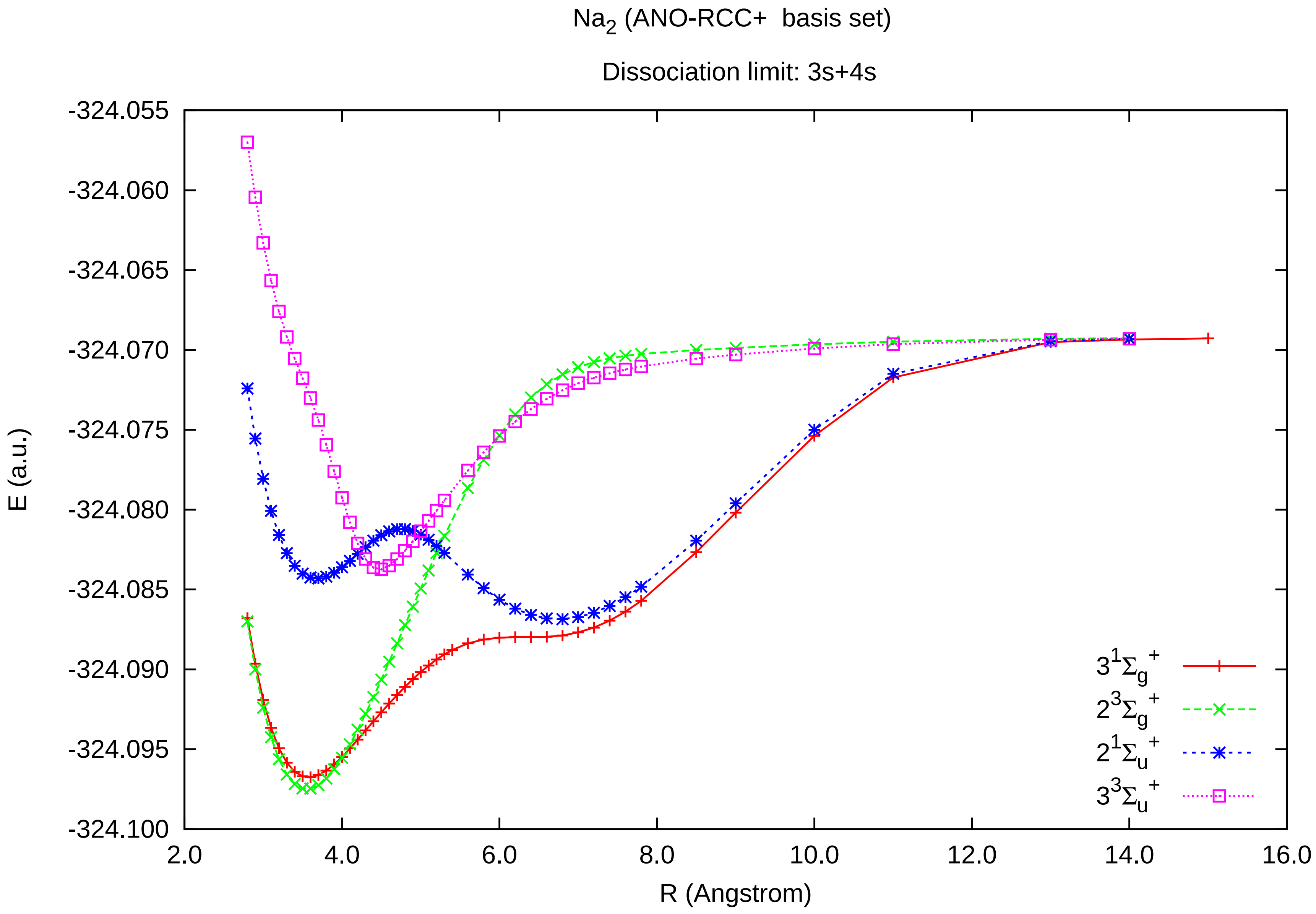
Na_2^{+2} system separates into two closed shell subunits (isoelectronic with Ne atom). Very convenient reference function.

DEA applications for alkali metal diatomics

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** (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**

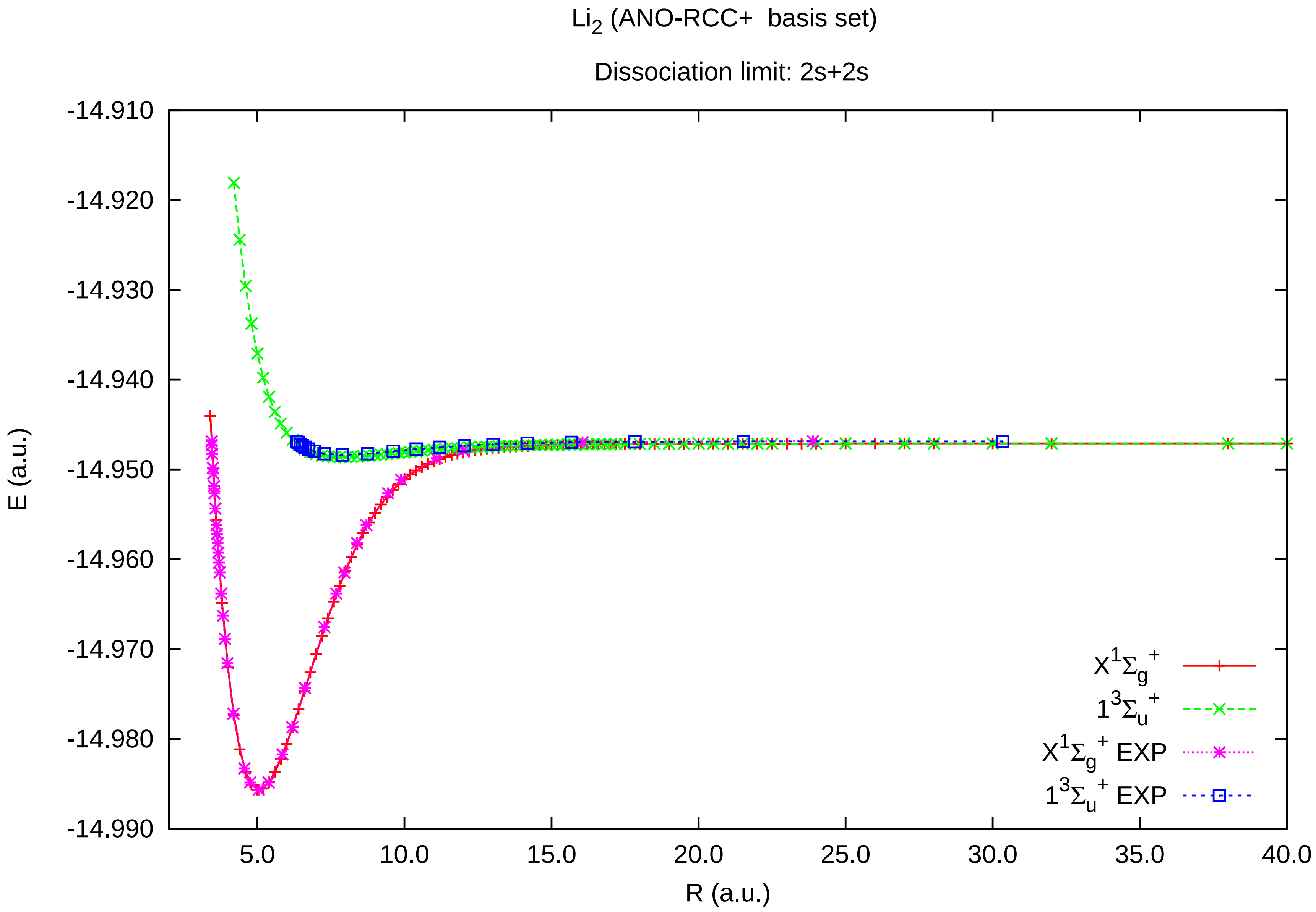


Na$_2$: ground state
(POL1 basis set; valence electrons were correlated)
-323.790
-323.800
-323.810
-323.820
-323.830
-323.840
-323.850
-323.860
-323.870
E (Hartrees)
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
R (Angstroms)
CCSD
CCSDT
CCSD(T)
DEA-EOM-CCSD
DEA-EOM-CCSDT'
DEA-EOM-CCSDT
IH-FS-CCSD (2,0)

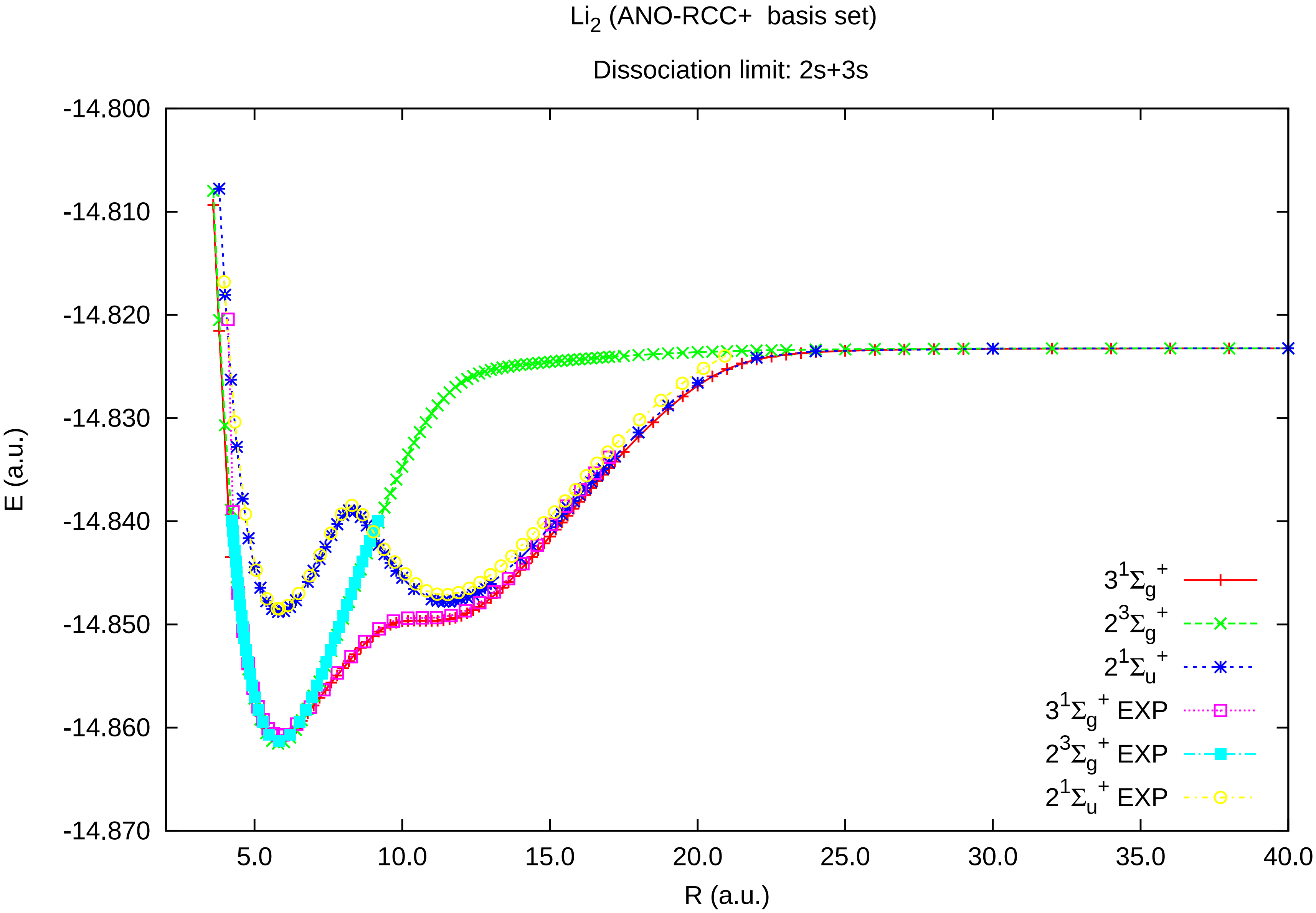

Na$_2$ (ANO-RCC+ basis set)
Dissociation limit: 3s+4s
E (a.u.)
-324.055
-324.060
-324.065
-324.070
-324.075
-324.080
-324.085
-324.090
-324.095
-324.100
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
R (Angstrom)
$3^1\Sigma_g^+$
$2^3\Sigma_g^+$
$2^1\Sigma_u^+$
$3^3\Sigma_u^+$

How can we prove that the obtained results are reliable?

- compare theoretical curves with experimental ones
- compare calculated vibrational energy levels with experiment
- calculate spectroscopic constants
  and compare with experiment


Li$_2$ (ANO-RCC+ basis set)
Dissociation limit: 2s+2s
E (a.u.)
R (a.u.)
-14.910
-14.920
-14.930
-14.940
-14.950
-14.960
-14.970
-14.980
-14.990
5.0
10.0
15.0
20.0
25.0
30.0
35.0
40.0
$X^1\Sigma_g^+$
$1^3\Sigma_u^+$
$X^1\Sigma_g^+$ EXP
$1^3\Sigma_u^+$ EXP

Sym.	R_e (Å)	Δ (Å)	D_e (cm^{-1})	Δ (cm^{-1})	ω_e (cm^{-1})	Δ (cm^{-1})	T_e (eV)	Δ (eV)
				2s + 2s dissociation limit				
$X^1\Sigma_g^+$	**2.676**	**0.003**	**8465**	**-52**	**350**	**-1**	**-**	**-**
exp.	**2.673**		**8517**		**351**		**-**	
$1^3\Sigma_u^+$	**4.170**	**-0.001**	**333**	**0**	**65**	**0**	**1.008**	**-0.006**
exp.	**4.171**		**333**		**65**		**1.014**	

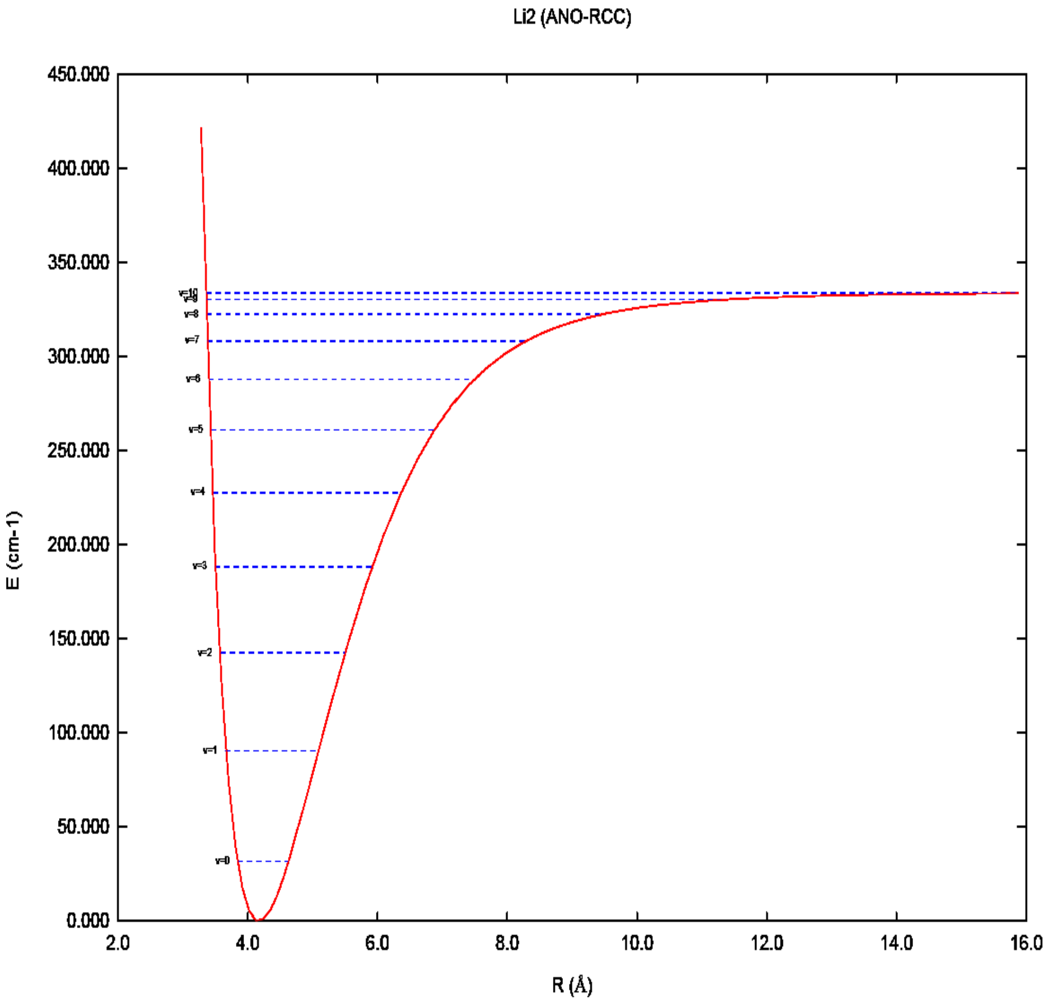


Li_2 (ANO-RCC+ basis set)
Dissociation limit: 2s+3s
E (a.u.)
-14.800
-14.810
-14.820
-14.830
-14.840
-14.850
-14.860
-14.870
R (a.u.)
5.0
10.0
15.0
20.0
25.0
30.0
35.0
40.0
$3^1\Sigma_g^+$
$2^3\Sigma_g^+$
$2^1\Sigma_u^+$
$3^1\Sigma_g^+$ EXP
$2^3\Sigma_g^+$ EXP
$2^1\Sigma_u^+$ EXP

Sym.	R_e (Å)	Δ (Å)	D_e (cm^{-1})	Δ (cm^{-1})	ω_e (cm^{-1})	Δ (cm^{-1})	T_e (eV)	Δ (eV)
2s + 3s dissociation limit								
$3^1\Sigma_g^+$ inner	3.088	0.002	8290	-23	240	-6	3.392	-0.006
exp.	3.086		8313		246		3.398	
$3^1\Sigma_g^+$ outer	5.652	-	5795	-	-	-	3.702	-
exp.	-		-		-		-	
$2^3\Sigma_g^+$	3.084	-0.006	8410	-	269	0	3.378	-
exp.	3.090		-		269		-	
$2^1\Sigma_u^+$ inner	3.094	-0.002	5608	-12	260	0	3.725	-0.007
exp.	3.096		5620		260		3.732	
$2^1\Sigma_u^+$ outer	6.088	0.051	5389	-10	118	-	3.752	-0.017
exp.	6.037		5399		-		3.769	
$3^3\Sigma_u^+$	3.676	-	5877	-	350	-	3.692	-
exp.	-		-		-		-	

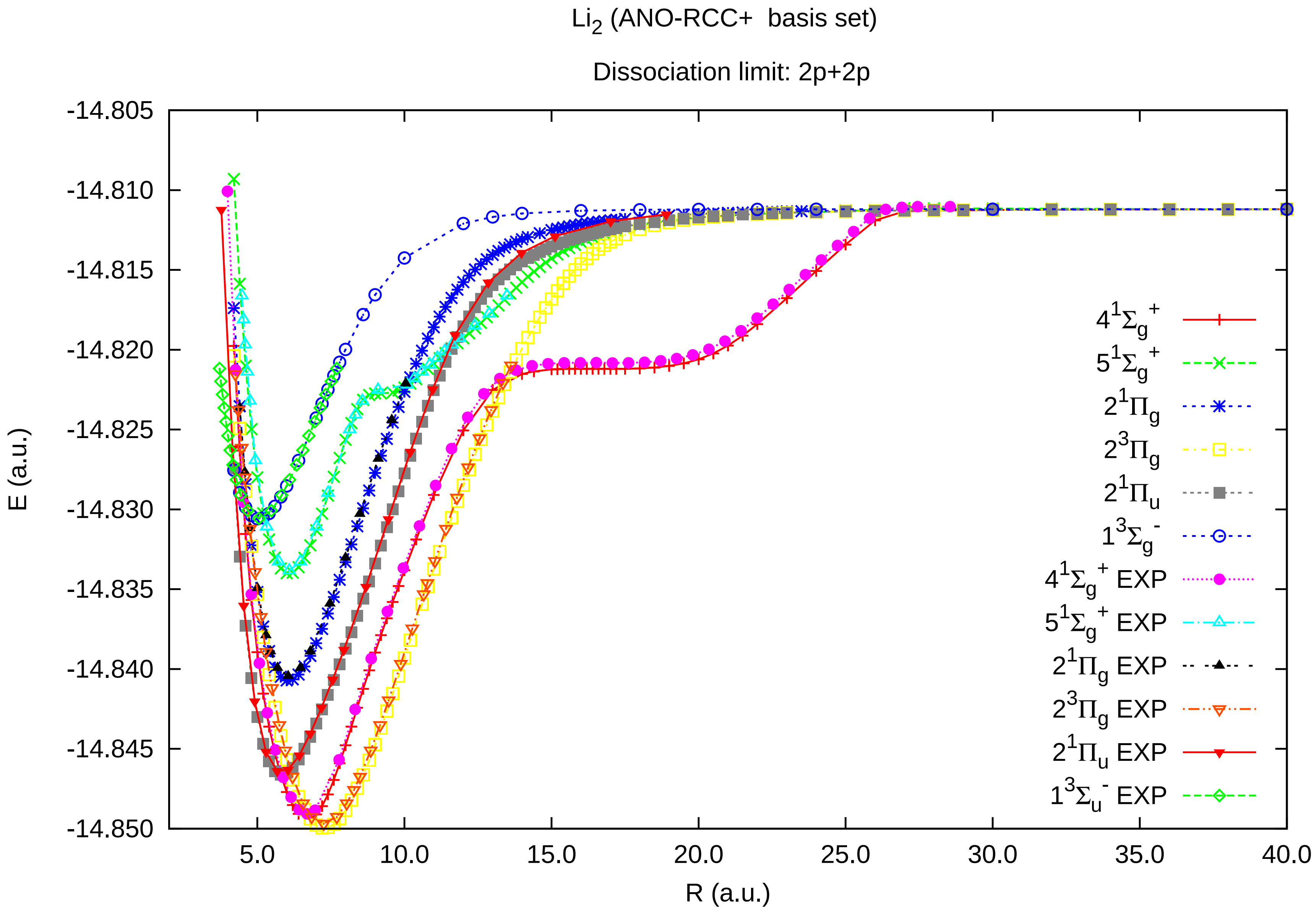
DEA calculations: $1^3\Sigma_u^+$ of Li$_2$

Vibrational levels



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

	E_v (cm^{-1})		
v	Theoretical	Δ	Exp.$^{b)}$
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	



Li_2 (ANO-RCC+ basis set)
Dissociation limit: 2p+2p
E (a.u.)
R (a.u.)
-14.805
-14.810
-14.815
-14.820
-14.825
-14.830
-14.835
-14.840
-14.845
-14.850
5.0
10.0
15.0
20.0
25.0
30.0
35.0
40.0
$4^1\Sigma_g^+$
$5^1\Sigma_g^+$
$2^1\Pi_g$
$2^3\Pi_g$
$2^1\Pi_u$
$1^3\Sigma_g^-$
$4^1\Sigma_g^+$ EXP
$5^1\Sigma_g^+$ EXP
$2^1\Pi_g$ EXP
$2^3\Pi_g$ EXP
$2^1\Pi_u$ EXP
$1^3\Sigma_u^-$ EXP

Sym.	R_e	Δ	D_e	Δ	ω_e	Δ	T_e	Δ
	($\AA$)	**(Å)**	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	**(eV)**	**(eV)**
				2p + 2p dissociation limit				
$4^1\Sigma_g^+$ **inner**	**3.547**	**-0.001**	**8380**	**31**	**225**	**-2**	**3.709**	**-0.007**
exp.	**3.548**		**8349**		**227**		**3.716**	
$^1\Sigma_g^+$ **outer**	**9.020**	**0.010**	**2197**	**-**	**24**	**-**	**4.476**	**-**
exp.	**9.010**		**-**		**-**		**-**	
$2^1\Pi_g$	**3.201**	**0.000**	**6481**	**26**	**230**	**0**	**3.944**	**-0.007**
exp.	**3.201**		**6455**		**230**		**3.951**	
$2^3\Pi_g$	**3.851**	**0.035**	**8505**	**21**	**187**	**-2**	**3.693**	**-0.007**
exp.	**3.816**		**8484**		**189**		**3.700**	
$2^1\Pi_u$	**3.086**	**0.005**	**7773**	**-1**	**237**	**-2**	**3.784**	**-0.004**
exp.	**3.081**		**7774**		**239**		**3.788**	
$1^1\Delta_g$	**2.913**	**-**	**5952**	**13**	**274**	**3**	**3.559**	**-**
exp.	**-**		**9579**		**271**		**-**	
$5^1\Sigma_g^+$ **inner**	**3.215**	**-0.005**	**5010**	**-**	**248**	**-**	**4.127**	**-0.004**
exp.	**3.220**		**-**		**-**		**4.131**	

Indirect application of electron affinity

EA-EOM-CC applications for EE calculations

Excitation energies (eV) for the Na atom in ANO-RCC+ basis set.

Sym.	**EA-EOM-CCSD** $GS\ n^6$ $EOM\ n^5$	Δ	**Exp.**
$^2P^0$ $(3p)$	**2.088**	**-0.014**	**2.102**
^2S $(4s)$	**3.172**	**-0.019**	**3.191**
^2D $(3d)$	**3.594**	**-0.023**	**3.617**
$^2P^0$ $(4p)$	**3.731**	**-0.022**	**3.753**
^2S $(5s)$	**4.097**	**-0.019**	**4.116**
MAE		**0.019**	

EA-EOM-CC applications for EE calculations

Excitation energies (eV) for the Li atom in ANO-RCC+ basis set.

Sym.	**EA-EOM-CCSD** $GS\ n^6$ $EOM\ n^5$	Δ	**Exp.**
$^2P^0\ (2p)$	**1.849**	**0.001**	**1.848**
$^2S\ (3s)$	**3.371**	**-0.002**	**3.373**
$^2P^0\ (3p)$	**3.834**	**-0.000**	**3.834**
$^2D\ (3d)$	**3.876**	**-0.003**	**3.879**
$^2S\ (4s)$	**4.340**	**-0.001**	**4.341**
MAE		**0.001**	

EOM-CC – summary

Closed shell system		Studied system
A^{-}	$\overrightarrow{\mathbf{IP-EOM}}$	**A**
A^{+}	$\overrightarrow{\mathbf{EA-EOM}}$	**A**
A^{-2}	$\overrightarrow{\mathbf{DIP-EOM}}$	**A**
A^{+2}	$\overrightarrow{\mathbf{DEA-EOM}}$	**A**
A^{+3}	$\overrightarrow{\mathbf{TEA-EOM}}$	**A**
$\vdots$	$\overrightarrow{\vdots}$	$\vdots$