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Multi-reference coupled-cluster study of the ionic-neutral curve crossing LiF

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The recently developed exponential multi-reference wavefunction ansatz [J. Chem. Phys. **123** (2005) 84102] and the single-reference formalism multi-reference coupled cluster ansatz [J. Chem. Phys. **94** (1991) 1229] are applied to calculate the potential energy surface of LiF. The avoided crossing region for the ionic and the covalent $^1\Sigma^+$ states are analysed using plain **self consistent field** and state averaged **complete active space** orbitals. Additionally, dipole moments are reported. All results are discussed and compared with full and **multi-reference configuration interaction** calculations.

I. INTRODUCTION

The ionic-neutral curve crossing of lithium fluoride is one of the major tests to check for a balanced treatment of static and dynamic correlation effects within an approximative solution of the Schrödinger equation. Therefore, it has been frequently used in the literature as a benchmark system. **Initially there were MCSCF and CI calculations of Kahn *et al.* [1], Botter *et al.* [2], and Werner *et al.* [3]. Later Spiegelmann *et al.* [4, 5] applied effective Hamiltonian techniques. In 1988 Bauschlicher *et al.* [6] published full CI calculations while in 1986 Adamowicz *et al.* [7] performed coupled cluster calculations at CCSD level. In 1990 Scuseria *et al.* [8] published CCSDT results. Later Nakano [9] and Nakano *et al.* [10] performed MCSCF based quasidegenerate perturbative calculations and second-order quasi-degenerate PT calculations, respectively. Finley *et al.* did multi-state CASPT2 [11] and DMRG calculations [12]. In 2003 Meller *et al.* [13] performed dressed MRCI while Legeza *et al.* [14] did DMRG calculations.** Recently multi-state MRPT calculations of Franz [15], Brueckner EOM-CC calculations of Nooijen *et al.* [16], decontracted MR calculations of Angeli *et al.* [17], approximate perturbative approaches of Angeli *et al.* [18], and hybrid DFT/CI calculations of Wu *et al.* [19] were carried out.

The lithium fluoride system is of certain interest as it involves an avoided crossing of the ground $X^1\Sigma^+$ state with the excited $1^1\Sigma^+$ state with the location of this crossing being very sensitive to the amount of correlation in the wavefunction. Additionally, the orbitals show a very strong dependence on the states as one state is ionic while the other is neutral. Therefore, one usually employs state averaged orbitals making the balanced description of ground and excited state easier. In order to challenge the MRCC approaches considered in this article we will additionally use closed shell SCF orbitals. In the vicinity of the equilibrium the latter allow a reasonable description of the ground $X^1\Sigma^+$ state while upon dissociation they naturally describe the ionic $1^1\Sigma^+$ state corresponding to $\text{Li}^+ + \text{F}^-$. Consequently, a balanced

description of both states becomes rather difficult.

For single-reference (SR) cases the coupled-cluster (CC) methods [20–22] are known to be insensitive to orbital rotations due to the presence of the $e^{\hat{T}_1}$ terms. In the multi-reference (MR) case this is less well established. Additionally, up to now the best formulation of an MRCC is yet to be found. Despite of many efforts the generalisation of the SRCC approach to an MR model space turned out to be a rather sophisticated task. There has been a wide variety of MRCC type ansätze with each having certain features and drawbacks. First of all the literature offers the state universal (SUMRCC) [23, 24] and valence universal (VUMRCC) ansätze [25–29]. Besides the "universal" approaches there are state selective MRCC (SSMRCC) methods. Among these are the dressed configuration interaction (CI) based ansätze of Malrieu and coworkers [30–32], SUMRCC based ansätze with a certain set of sufficiency conditions applied by Li and Paldus [33, 34], and reduced multi-reference (RMR)-CC ansätze by Li and Paldus [35–37]. State specific variants of the SUMRCC approach have been proposed by Mukherjee and coworkers [38, 39] Pittner, Hubac and coworkers [40–42] (Brillouin-Wigner type ansätze).

In this paper we report results for the SRCC based state specific ansatz of Oliphant and Adamowicz (SRMRCC) [43] and Piecuch *et al.* [44] and the MRexpT ansatz of Hanrath [45, 46] in application to lithium fluoride (LiF). The SRMRCC ansatz can be interpreted as a conventional SRCC method with additional (incomplete) higher excitations in the cluster operator \hat{T} and corresponding projections to span an MR space upon linearization of the exponential. However, although usually very accurate with respect to the energy, the approach is symmetry broken and fails to produce smooth potential surfaces. Recently [47] spin projection and state overlap errors were studied for N_2 . There are also recent attempts to partially cure the symmetry breaking within the SRMRCC ansatz [48]. The MRexpT ansatz is a state specific variant of the state universal approach of Jeziorzki and Monkhorst. The MRexpT has been reported to be as accurate as the SRMRCC approach [45–47, 49, 50] while it does not suffer from a symmetry problem. MRexpT is size consistent [45] and has been recently shown [50] to be core but not valence connected.

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The paper is organised as follows: After a brief presentation of the SRMRCC and MRexpT approaches the results section reports on the calculation of LiF with SCF and state averaged CASSCF orbitals reporting the energy differences to full CI including a comparison with MRCI. Additionally calculations of the dipole moment have been carried out as the latter is very sensitive to deficiencies of the wavefunction in the vicinity of the avoided crossing region.

II. MRCC ANSÄTZE

A. SRMRCC

The single reference based ansatz (SRMRCC) of Adamowicz *et al.* [43] and Piecuch *et al.* [44] uses the conventional single-reference coupled cluster wavefunction ansatz

$$|\Psi\rangle = e^{\hat{T}}|0\rangle \quad (1)$$

with $|0\rangle$ a single determinant and

$$\hat{T} = \sum_i t_i \hat{\tau}_i \quad (2)$$

with t_i and $\hat{\tau}_i$ amplitudes and substitution operators, respectively. Its cluster operators \hat{T} contain additional excitations on top of e.g. singles and doubles in order to span a multi-reference space according to $(1+\hat{T})|0\rangle$ spanning the same space as $|\Psi_{\text{MRCI}}\rangle$ (assuming $|0\rangle$ in $|\Psi_{\text{MRCI}}\rangle$ not to vanish). Using the linked (similarity transformed) form of the coupled cluster equations the SRMRCC ansatz inherits its full connectivity from its parent single-reference coupled cluster method. Although in many cases energetically very accurate the SRMRCC ansatz suffers from the problem of symmetry breaking and missing universality over a full potential surface as it requires a particular Fermi vacuum. Later variants of the SRMRCC ansatz [48, 51–54] do not entirely solve this fundamental problem of the SRMRCC approach.

B. MRexpT

The MRexpT ansatz [45, 46] is based on the state universal ansatz [23] and uses a reference specific cluster operator. The wave function ansatz is given by

$$|\Psi\rangle = \sum_{\mu} c_{\mu} e^{\hat{T}_{\mu}} |\mu\rangle \quad (3)$$

with $|\mu\rangle$ the reference determinants, $c_{|\mu\rangle}$ the associated coefficients, and the cluster operators

$$\hat{T}_{\mu} = \phi(c_{\mu}) \sum_{\hat{\tau}_{\mu,i} \in \mathbb{T}_{\mu}} t_{\hat{\tau}_{\mu,i}} \hat{\tau}_{\mu,i}. \quad (4)$$

The major difference of equation Eq. (4) to the state universal coupled-cluster formalism is the amplitude index replacement of $t_{\hat{\tau}_{\mu,i}}$ by $t_{\hat{\tau}_{\mu,i}|\mu}$ with the sign rule $t_{-|\beta\rangle} = -t_{|\beta\rangle}$ applied switching from an excitation based to a determinant based indexing. This removes any amplitude ambiguity problems and causes the MRexpT Ansatz to be state selective. The reference phase compensation factor $\phi(z)$ is given by $\phi(z) = e^{-i \arg z}$, $z \in \mathbb{C}$, and guarantees the potential completeness of equation Eq. (3) and does not introduce any new degree of freedom.

Upon insertion of equation Eq. (3) into the Schrödinger equation we get

$$\hat{H} \sum_{\mu} c_{\mu} e^{\hat{T}_{\mu}} |\mu\rangle = E \sum_{\mu} c_{\mu} e^{\hat{T}_{\mu}} |\mu\rangle \quad (5)$$

with \hat{H} the Hamilton operator and E the energy eigenvalue. Projecting equation Eq. (5) from the left onto $\langle \rho | \in (\mathbb{P} \cup \mathbb{Q})^{\dagger}$ we obtain a system of equations linear in the reference coefficients c_{μ} and non linear in the amplitudes $t_{|\alpha\rangle}$

$$\sum_{\mu} c_{\mu} \langle \rho | \hat{H} - E | e^{\hat{T}_{\mu}} \mu \rangle = 0, \quad \forall \langle \rho |. \quad (6)$$

The remaining additional variable E is fixed by the norm of the reference coefficients by

$$\sum_{\mu} |c_{\mu}|^2 = 1 \quad (7)$$

which corresponds to a straightforward generalisation of the intermediate normalisation. Equations Eq. (6) and Eq. (7) together form a set of $\text{ord}(\mathbb{P}) + \text{ord}(\mathbb{Q}) + 1$ equations for the unknowns c_{μ} and $t_{\hat{\tau}_{\mu,i}|\mu}$ and E respectively.

MRexpT has been shown to be size consistent [45] and core but not valence connected [50].

III. AVOIDED CROSSING OF LITHIUM FLUORIDE

As already pointed out in the introduction the LiF molecule has been frequently studied in the literature by various groups [1–19]. The ionic and covalent states of $^1\Sigma^+$ symmetry assemble an avoided crossing for an inter-atomic distance of ~ 11.5 a.u. inhibiting a single reference description. Close to the equilibrium the dominating configuration of the $X^1\Sigma^+$ ground state (ionic) of LiF is given by $|1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4\rangle$ while the $1^1\Sigma^+$ first excited state (covalent) is given by $|1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1 5\sigma^1 1\pi^4\rangle$. The 4σ and 5σ orbitals refer to F $2p\sigma$ and Li $2s$ orbitals respectively [6].

A. Calculation Details

In this article we adopt to the $(9s5p)/[4s2p]$ basis for Li and $(9s6p1d)/[4s3p1d]$ basis for F according to [6, 14]. We employed two different sets of orbitals:

$R/\text{a.u.}$	CAS avg. orbitals		SCF orbitals	
	$X^1\Sigma^+$ ^a	$1^1\Sigma^+$ ^a	$X^1\Sigma^+$ ^a	$1^1\Sigma^+$ ^a
2.95	$4\sigma^2$	$4\bar{\sigma}5\sigma$	$4\sigma^2$	$4\bar{\sigma}5\sigma$
\vdots	\vdots	\vdots	\vdots	\vdots
11.00	$4\sigma^2$	$4\bar{\sigma}5\sigma$	$4\sigma^2$	$4\bar{\sigma}5\sigma$
11.25	$4\sigma^2$	$4\sigma^2$	$4\sigma^2$	$4\bar{\sigma}5\sigma$
11.50	$4\sigma^2$	$4\sigma^2$	$4\sigma^2$	$4\bar{\sigma}5\sigma$
12.00	$4\bar{\sigma}5\sigma$	$4\sigma^2$	$4\sigma^2$	$4\bar{\sigma}5\sigma$
12.50	$4\bar{\sigma}5\sigma$	$4\sigma^2$	$4\bar{\sigma}5\sigma$	$4\sigma^2$
13.70	$4\bar{\sigma}5\sigma$	$4\sigma^2$	$4\bar{\sigma}5\sigma$	$4\sigma^2$

^aoccupations besides $|1\sigma^2 2\sigma^2 3\sigma^2 \dots 1\pi^4\rangle$

TABLE I: Varying orbital occupation in dominating determinants (Fermi vacua) for SRMRCC calculations

- (i) State averaged ($X^1\Sigma^+$ and $1^1\Sigma^+$) CAS($2e^-$, $4\sigma 5\sigma$) orbitals
- (ii) and closed shell SCF orbitals.

One should note that the closed shell SCF orbitals dissociate naturally into the ionic $\text{Li}^+ + \text{F}^-$ fragments and it remains a non-trivial task to assemble the wavefunction of the covalent ground state upon dissociation into $\text{Li} + \text{F}$.

All MRCI, SRMRCC, and MRexpT calculations were carried out with the natural CAS($2e^-$, $4\sigma 5\sigma$) reference space assembling four determinants corresponding to three singlet configuration state functions (CSFs) and one triplet CSF (with $S_z = 0$). Keeping the $1s$ and $2s$ of fluorine and the $1s$ of lithium frozen 6 electrons were correlated.

The SRMRCC calculations rely on the explicit choice of the Fermi vacuum. It has been chosen as the dominant determinant from the MRCI calculations and is given in Table I. Since only the 4σ and 5σ orbitals change in occupation only those are shown explicitly in table I. The remaining orbitals $1\sigma^2 2\sigma^2 3\sigma^2 \dots 1\pi^4$ stay doubly occupied.

The integral, SCF, CAS, MO transformation calculations were carried out using MOLCAS [55] with an additional interface [56].

B. Results for state averaged orbitals

First we discuss the results for the state averaged orbitals. Table II shows the results of the calculations. For reference it contains the state averaged CAS and full CI energies. The MRCI, SRMRCC and MRexpT results are given with respect to the full CI results. Figure 1 shows the absolute energies graphically with a closeup of the

avoided crossing region. Figure 2 shows the errors of MRCI, SRMRCC and MRexpT with respect to full CI.

In the discussion we shall consider the $X^1\Sigma^+$ ground state first. From the table and graphs we see MRCI to have the largest errors as expected although in terms of the NPE it performs reasonably. Interestingly the largest deviations from full CI appear neither for the equilibrium nor for the avoided crossing region but for the intermediate distances. Far from the avoided crossing region the absolute errors of SRMRCC are more than an order of magnitude smaller than those of MRCI while they are only a factor of 3 smaller in the avoided crossing region. Obviously, there is a significant discontinuity in the energy surface from $R = 11.5$ a.u. to $R = 12$ a.u. due to the change of the Fermi vacuum as can be seen from table I. There is no way to prevent the discontinuity as the Fermi vacuum has to be switched passing through the avoided crossing. Since there is no possibility to choose the optimal switching point without knowing the full CI results in advance we decided to switch the vacuum depending on the dominating determinant from the MRCI calculation. In contrast to SRMRCC the errors of MRexpT are apart from the crossing region somewhat larger but stay rather constant except for very short distances. Naturally, as MRexpT treats all references on the same footing there is no specific vacuum and there is no discontinuity.

For the $1^1\Sigma^+$ excited state the MRCI results are qualitatively very similar although the maximum errors do now occur for larger distances. The errors of SRMRCC are behaving in a complementary way to the $X^1\Sigma^+$ ground state. They are very small in comparison to MRCI in the vicinity of the avoided crossing and thereafter while they are significantly larger for the remaining distances. Since the two states change their character during the avoided crossing SRMRCC seems to give more accurate results for the covalent state. Once more there is a discontinuity in the energy now from $R = 11$ a.u. to $R = 11.25$ a.u. which corresponds to the change of the Fermi vacuum as can be seen from table I. MRexpT shows a very similar behaviour to the ground state. The errors remain rather constant at about $2 mE_h$ with a little decrease for $R = 13.7$ a.u.

The explicit discussion of the errors is summarised by the non-parallelity errors (NPEs) of the individual methods. The NPEs for the ground state read 3877, 2268, and 2063 a.u. for MRCI, SRMRCC, and MRexpT respectively while the corresponding values for the excited state are 4045, 3196, and 1470 a.u. Consequently, for the ground state the NPEs of SRMRCC and MRexpT are about a factor of 2 smaller than for MRCI. For the excited state the picture slightly differs as the NPE of SRMRCC is about 3/4 of that of MRCI while that of MRexpT is about 1/3 of that of MRCI.

Besides the calculation of the energy we evaluated the dipole moments of the wavefunction. The results are given in table III and figure 3. Since the dipole moment of the LiF molecule may be interpreted as a mea-

$R/a.u.$	$X^1\Sigma^+$					$1^1\Sigma^+$				
	CAS avg. ^a	FCI ^a	MRCI ^b	SRMRCC ^b	MReXPt ^b	CAS avg. ^a	FCI ^a	MRCI ^b	SRMRCC ^b	MReXPt ^b
2.95	-0.935 040	-1.114 140	8303	516	871	-0.738 142	-0.866 595	5914	1948	1979
3.05	-0.935 910	-1.115 217	8403	540	946	-0.743 960	-0.872 691	5967	1968	2006
3.15	-0.935 300	-1.114 826	8502	564	1019	-0.748 518	-0.877 566	6025	1992	2035
4.5	-0.881 719	-1.063 713	9697	784	1816	-0.766 009	-0.900 086	6671	2239	2321
5.5	-0.844 072	-1.024 631	10117	719	2120	-0.769 089	-0.906 181	6783	2272	2365
6.5	-0.817 536	-0.994 753	10163	640	2235	-0.771 073	-0.911 066	6756	2244	2351
7.5	-0.800 390	-0.972 336	10099	614	2243	-0.769 791	-0.914 503	6671	2191	2315
8.5	-0.792 592	-0.955 207	10023	617	2217	-0.762 861	-0.916 581	6601	2148	2284
9.5	-0.790 344	-0.941 815	9926	621	2221	-0.753 038	-0.917 701	6583	2135	2279
10	-0.789 965	-0.936 192	9851	614	2264	-0.748 189	-0.918 019	6611	2150	2294
10.5	-0.789 773	-0.931 167	9719	587	2365	-0.743 617	-0.918 211	6701	2198	2333
11	-0.789 677	-0.926 697	9400	501	2578	-0.739 365	-0.918 269	6982	2345	2424
11.25	-0.789 648	-0.924 684	9037	394	2749	-0.737 360	-0.918 220	7328	-851	2506
11.5	-0.789 628	-0.922 864	8405	176	2934	-0.735 435	-0.918 067	7943	-563	2622
12	-0.789 606	-0.920 307	6896	2444	2645	-0.731 808	-0.916 925	9423	325	2685
12.5	-0.789 595	-0.919 524	6402	2040	2244	-0.728 462	-0.914 307	9891	674	2121
13.7	-0.789 592	-0.919 261	6286	1950	2021	-0.721 417	-0.907 444	9959	759	1215
NPE			3877	2268	2063			4045	3196	1470

^aEnergies in $E_h + 106$

^bEnergies relative to full CI in μE_h

TABLE II: Energies for CAS($2e^-$, 4σ 5σ) orbitals, state averaged for two states

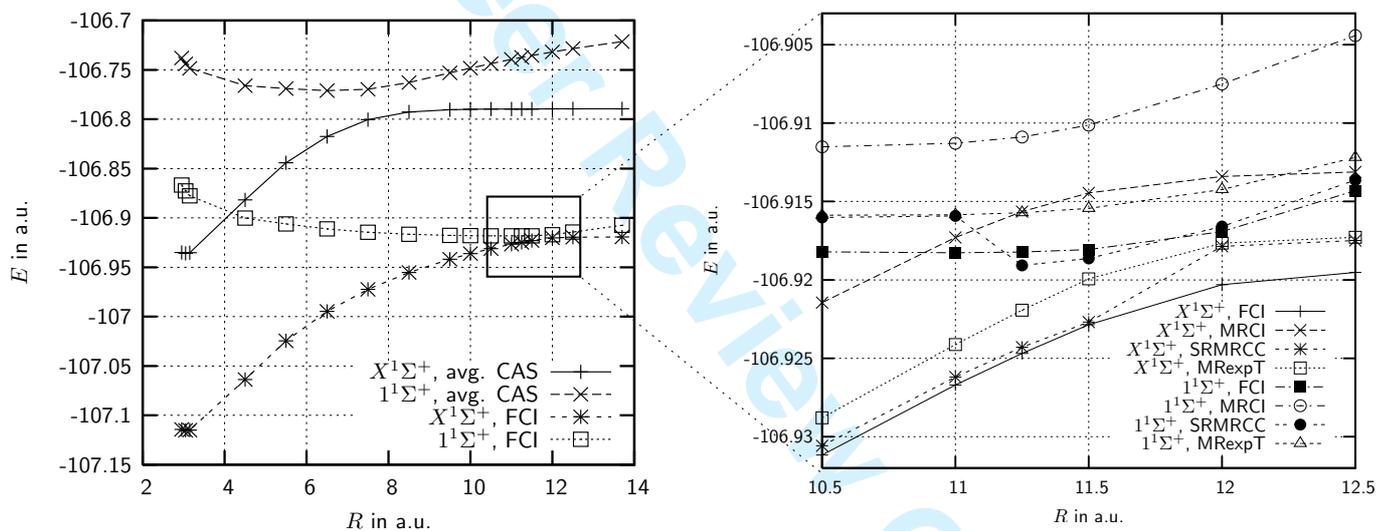


FIG. 1: Potential energy surface for CAS($2e^-$, 4σ 5σ) orbitals, state averaged for two states

sure of its ionicity it directly reflects the character of the given state. Figure 3 shows the smooth transition from the ionic to the covalent character of the ground and excited state. Consequently, the dipole moment and the relative position of its change with respect to full CI reflects the location of the avoided crossing. The size of the dipole moment is mainly governed by the weights of the ionic ($|1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4\rangle$) and covalent reference ($|1\sigma^2 2\sigma^2 3\sigma^2 \{4\sigma 5\bar{\sigma}\} 4\bar{\sigma} 5\sigma\rangle 1\pi^4\rangle$) determinants. As can be seen from figure 1 the position of the avoided crossing for the CAS calculations appears at about $R = 8$ a.u.

while for full CI it appears rather at $R = 12$ a.u. which is quite a difference. We conclude that the weights and the location of the avoided crossing are very sensitive to the amount of dynamical correlation in the wavefunction.

Since the dipole moment changes rather rapidly around the avoided crossing the errors in table III become rather large. From figure 3 we see MRCI, SRMRCC, and MReXPt (in that order) to approach the shape of the full CI dipole moment. Consequently, in table III MRCI shows the largest errors. The errors for SRMRCC are already smaller while they become still smaller for MReXPt. Far

$R/a.u.$	$X^1\Sigma^+$				$1^1\Sigma^+$			
	FCI ^a	MRCI ^b	SRMRCC ^b	MRexpT ^b	FCI ^a	MRCI ^b	SRMRCC ^b	MRexpT ^b
2.95	2.631	41	-14	-9	-1.445	-13	-8	-9
3.05	2.718	42	-15	-8	-1.437	-13	-8	-9
3.15	2.804	43	-16	-8	-1.427	-13	-8	-10
4.5	3.995	59	-30	-5	-1.134	9	0	-1
5.5	4.956	60	-37	0	-0.737	85	30	29
6.5	5.960	37	-42	2	-0.323	153	59	58
7.5	6.978	-1	-48	0	-0.016	178	74	73
8.5	7.988	-58	-60	-4	0.181	199	93	87
9.5	8.954	-172	-90	-13	0.341	278	143	126
10	9.390	-308	-131	-25	0.448	399	212	179
10.5	9.739	-640	-233	-59	0.632	717	385	302
11	9.833	-1736	-577	-205	1.065	1800	960	663
11.25	9.601	-3070	-1058	-474	1.558	3128	1082	1086
11.5	8.852	-4711	-1989	-1236	2.567	4764	2086	1747
12	3.990	-2983	-2474	-2073	7.946	3027	2034	1301
12.5	0.790	-506	-406	-380	11.660	541	308	97
13.7	0.059	-22	-15	-16	13.614	43	-3	-10

^aDipole moment in a.u.

^bDipole moment relative to full CI in 10^{-3} a.u.

TABLE III: Dipole moments for CAS($2e^-$, $4\sigma 5\sigma$) orbitals, state averaged for two states

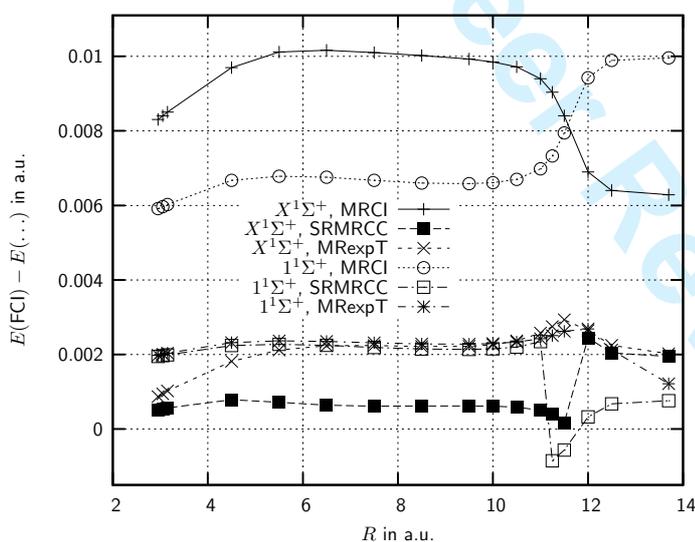


FIG. 2: Potential energy surface differences for CAS($2e^-$, $4\sigma 5\sigma$) orbitals, state averaged for two states, $E(\dots)$ denoting the energies of the various methods

from the crossing all considered correlation approaches perform very reasonably. The $X^1\Sigma^+$ and $1^1\Sigma^+$ states behave qualitatively very similar.

C. Results for closed shell SCF orbitals

In this section we consider the results for the closed shell SCF orbitals. As mentioned in the introduction the closed shell SCF corresponds to the ionic

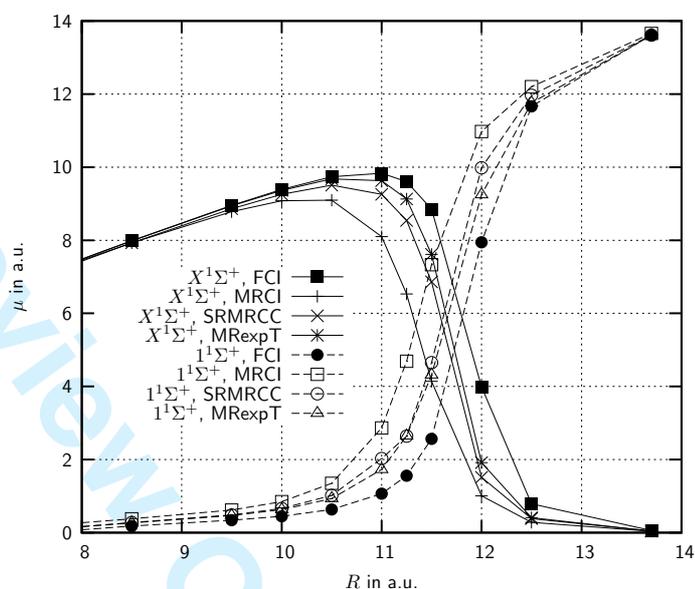


FIG. 3: Dipole moments for CAS($2e^-$, $4\sigma 5\sigma$) orbitals, state averaged for two states

$[1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4]$ occupation. In contrast to the state averaged orbitals such orbitals "prefer" the ionic state and it is a difficult task for the truncated correlation approaches MRCI, SRMRCC, and MRexpT (unlike full CI) to recover from those orbitals for the covalent state.

Table IV shows the numerical results of the calculations. Figure 4 shows the absolute energies graphically once again with a closeup of the avoided crossing region while figure 5 shows the relative errors of MRCI, SRM-

$R/a.u.$	SCF ^a	$X^1\Sigma^+$				$1^1\Sigma^+$			
		FCI ^a	MRCI ^b	SRMRCC ^b	MReXP ^b	FCI ^a	MRCI ^b	SRMRCC ^b	MReXP ^b
2.95	-0.964 474	-1.115 283	6363	2782	2816	-0.861 818	18260	4941	4427
3.05	-0.965 001	-1.116 316	6478	2850	2888	-0.868 001	18095	4840	4443
3.15	-0.964 063	-1.115 881	6596	2920	2963	-0.872 961	17944	4745	4456
4.5	-0.907 009	-1.064 282	8015	3856	3952	-0.896 557	16597	3967	4382
5.5	-0.866 241	-1.024 986	8535	4210	4316	-0.903 185	16164	3756	4267
6.5	-0.836 226	-0.995 025	8672	4272	4377	-0.908 281	15962	3707	4196
7.5	-0.814 302	-0.972 601	8609	4188	4294	-0.911 761	15609	3659	4063
8.5	-0.797 762	-0.955 485	8481	4071	4180	-0.913 858	15074	3553	3854
9.5	-0.784 839	-0.942 094	8360	3962	4080	-0.915 029	14476	3391	3621
10	-0.779 381	-0.936 459	8314	3908	4038	-0.915 388	14183	3295	3511
10.5	-0.774 464	-0.931 404	8282	3843	3998	-0.915 638	13899	3192	3412
11	-0.770 012	-0.926 863	8274	3735	3956	-0.915 793	13619	3078	3325
11.25	-0.767 941	-0.924 773	8287	3631	3930	-0.915 833	13474	3015	3287
11.5	-0.765 965	-0.922 803	8321	3433	3897	-0.915 840	13314	2943	3249
12	-0.762 270	-0.919 318	8566	5478	3810	-0.915 643	12840	2730	3130
12.5	-0.758 884	-0.917 210	9832	2508	3288	-0.914 365	11372	3415	3218
13.7	-0.751 801	-0.916 611	12893	2296	3464	-0.907 858	7924	3835	3853
NPE			6530	3182	1561		10336	2211	1326

^aEnergies in $E_h + 106$

^bEnergies relative to full CI in μE_h

TABLE IV: Energies for closed shell SCF orbitals

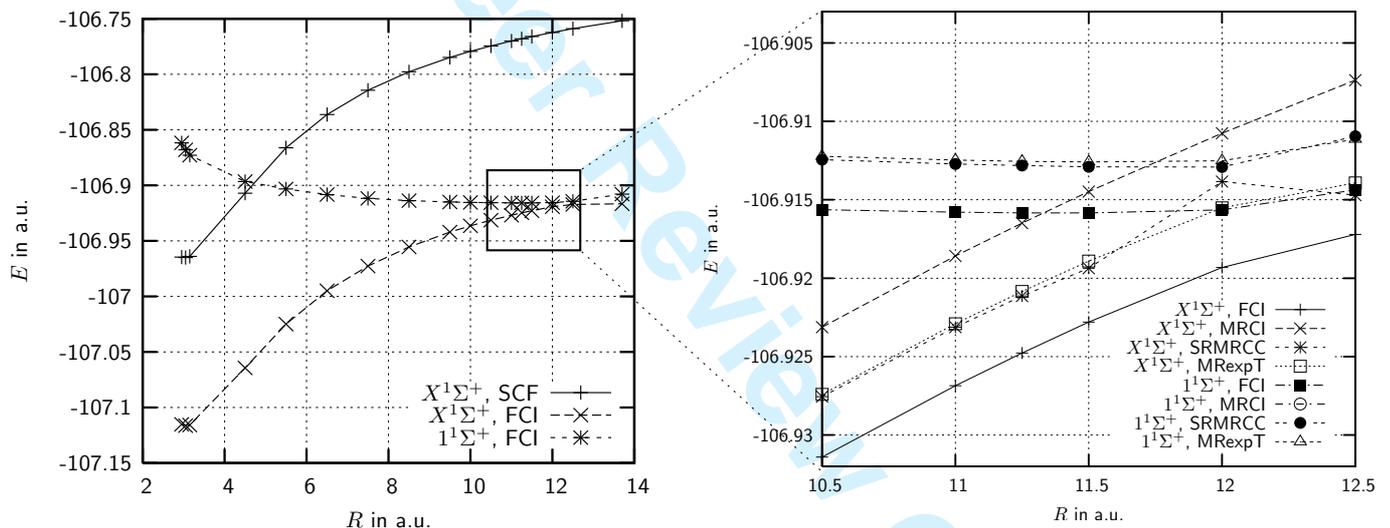


FIG. 4: Potential energy surface for closed shell SCF orbitals

RCC and MReXP^T with respect to full CI.

Considering the $X^1\Sigma^+$ ground state first MRCI shows errors of a similar order of magnitude as for the state averaged orbitals. The largest errors however occur now for large distances after the state crossing showing the significant dependence of MRCI on the choice of the orbitals. Due to the larger variation of the errors along the potential energy surface the NPE becomes roughly twice as large (6530 vs. 3877 a.u.). The behaviour of SRMRCC is almost complementary. The absolute errors increase significantly while the NPE increases only mod-

erately (3182 vs. 2268 a.u.). This is due to the fact that the previously very high accuracy of SRMRCC for small distances has been removed. The NPE is mostly dominated by the error of 5478 μE_h at $R = 12$ a.u. Actually, according to table I this is also the location of the change of the Fermi vacuum from $R = 12$ to $R = 12.5$ a.u. and the location of the discontinuity. Considering MReXP^T the overall average errors also become larger while the NPE decreases (1561 vs. 2063 a.u.). This is due to a less accurate description in the vicinity of the equilibrium similarly to SRMRCC making the distance between best

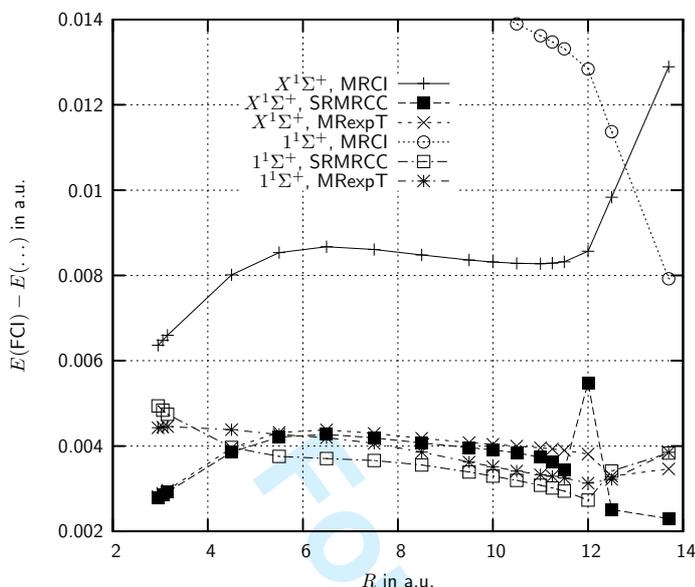


FIG. 5: Potential energy surface differences for closed shell SCF orbitals, $E(\dots)$ denoting the energies of the various methods

and worst errors smaller. However, the NPE of MRexpT fully benefits from this effect as MRexpT does not suffer from a discontinuity problem as SRMRCC does.

Considering the $1^1\Sigma^+$ excited state we see the accuracy of MRCI seriously affected by the closed shell SCF orbitals. While the error after the crossing (with the ionic state to be described) becomes reasonable ($7924 \mu E_h$ at $R = 13.7$ a.u.) it gets very large for $R < 13.7$ for the covalent state. The maximum error of $18260 \mu E_h$ at $R = 2.95$ a.u. results in a very large NPE of $10336 \mu E_h$ (vs. $4045 \mu E_h$ for the state averaged CAS orbitals). In contrast to MRCI the coupled cluster type methods are much less sensitive to the choice of the orbitals. SRMRCC shows a good performance with a moderate discontinuity and an NPE of $2211 \mu E_h$ (vs. $3196 \mu E_h$ for the state averaged CAS orbitals). MRexpT performs very good with rather constant deviations from full CI leading to a very small NPE of $1326 \mu E_h$ (vs. $1470 \mu E_h$ before).

Finally we discuss the dipole moments for closed shell SCF orbitals as shown in table V and figure 6. As can be seen from figure 6 (and also figure 5) the state flip for MRCI is delayed to larger R and the errors within the dipole moment become rather large. Besides from its discontinuity for the $X^1\Sigma^+$ ground state dipole moment from $R = 11.5$ to $R = 12$ a.u. SRMRCC behaves reasonably. MRexpT shows no discontinuities and has smaller errors for $R \leq 12$ a.u. but larger errors for $R > 12$ a.u. than SRMRCC.

To summarise the MRCC results are to a large extent independent from the choice of the orbitals. Actually, in terms of the NPE the results turned out to be more accurate for the closed shell SCF orbitals than for the state averaged orbitals. This result is of course not to be

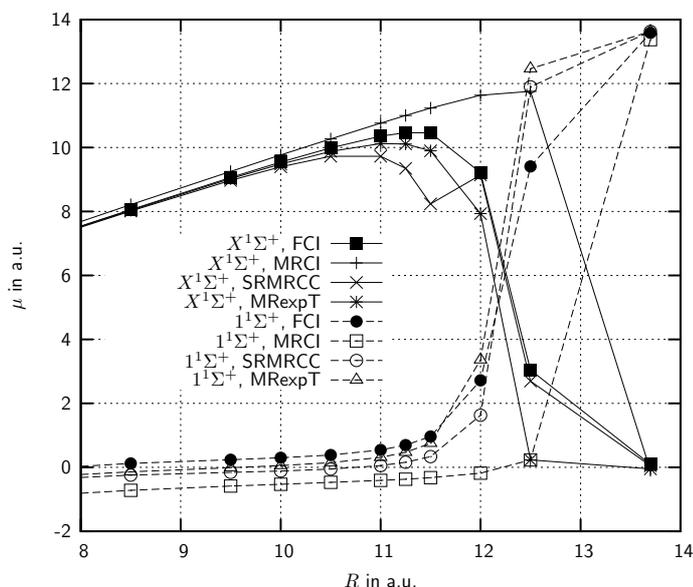


FIG. 6: Dipole moments for closed shell SCF orbitals

generalised in the sense that SCF orbitals are the best for MRCC calculations. What we should learn from the calculations and the previous analysis is that SRMRCC and MRexpT seem to preserve the orbital insensitivity of SRCC to the MR case for this rather difficult test.

IV. CONCLUSION

We reported on MRCI, SRMRCC, and MRexpT results of the ionic-neutral curve crossing of lithium fluoride. The comparison was made with respect to full CI rather than experimental results. The primary goal of this study was to test and challenge the MRCC approaches in difficult cases. This is especially true for the use of closed shell SCF orbitals. In addition to the energy the comparison included the calculation of the dipole moment.

Both MRCC approaches provide a significantly higher accuracy than the MRCI approach especially if closed shell SCF orbitals are employed. It is expected that this superiority increases substantially for a growing number of electrons.

To summarise the overall performance of MRexpT is slightly better than that of SRMRCC. The most severe problem of SRMRCC seems to be its symmetry breaking. This deficiency is mostly apparent if the dominant determinant changes along a potential energy surface causing discontinuities in the properties. However, this principle problem is already present within any single point calculation.

$R/\text{a.u.}$	$X^1\Sigma^+$				$1^1\Sigma^+$			
	FCI ^a	MRCI ^b	SRMRCC ^b	MRexpT ^b	FCI ^a	MRCI ^b	SRMRCC ^b	MRexpT ^b
2.95	2.636	11	-4	-4	-1.458	-604	-250	-171
3.05	2.723	12	-4	-4	-1.449	-604	-248	-174
3.15	2.810	13	-5	-4	-1.438	-605	-246	-176
4.5	4.010	36	-9	-6	-1.140	-620	-216	-193
5.5	4.979	67	-11	-4	-0.746	-702	-237	-218
6.5	5.994	101	-16	-3	-0.343	-800	-281	-247
7.5	7.026	130	-26	-6	-0.054	-846	-328	-261
8.5	8.056	155	-46	-16	0.120	-842	-366	-258
9.5	9.063	189	-92	-40	0.235	-823	-395	-246
10	9.544	221	-146	-65	0.296	-825	-411	-240
10.5	9.990	280	-267	-115	0.382	-853	-436	-236
11	10.354	409	-627	-231	0.545	-952	-488	-234
11.25	10.462	539	-1113	-351	0.697	-1067	-540	-230
11.5	10.455	776	-2215	-561	0.964	-1290	-631	-212
12	9.215	2419	-74	-1283	2.721	-2905	-1092	637
12.5	3.043	8714	-349	-2808	9.406	-9173	2490	3055
13.7	0.090	-187	-41	-137	13.582	-212	45	42

^aDipole moment in a.u.

^bDipole moment relative to full CI in 10^{-3} a.u.

TABLE V: Dipole moments for closed shell SCF orbitals

Acknowledgments

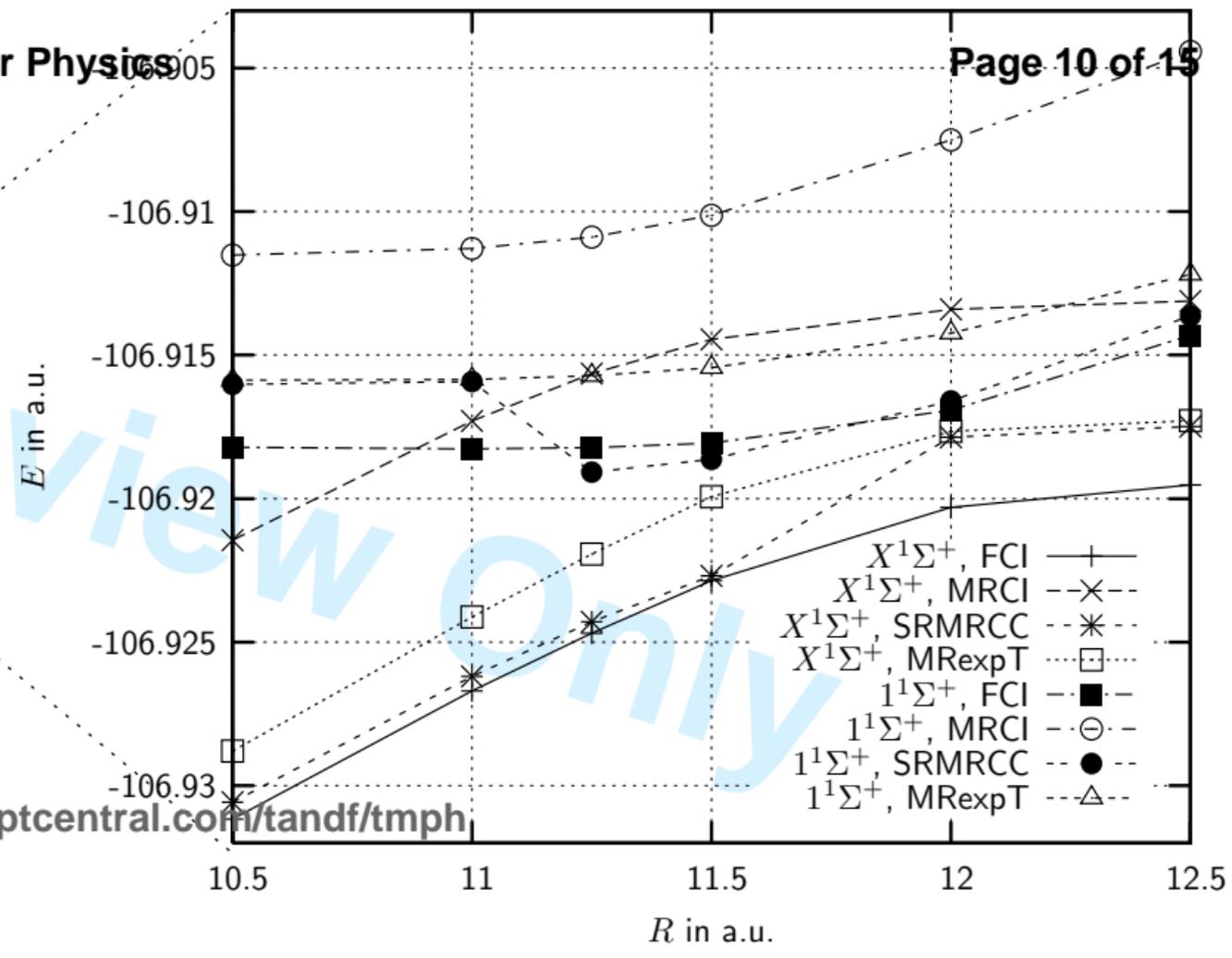
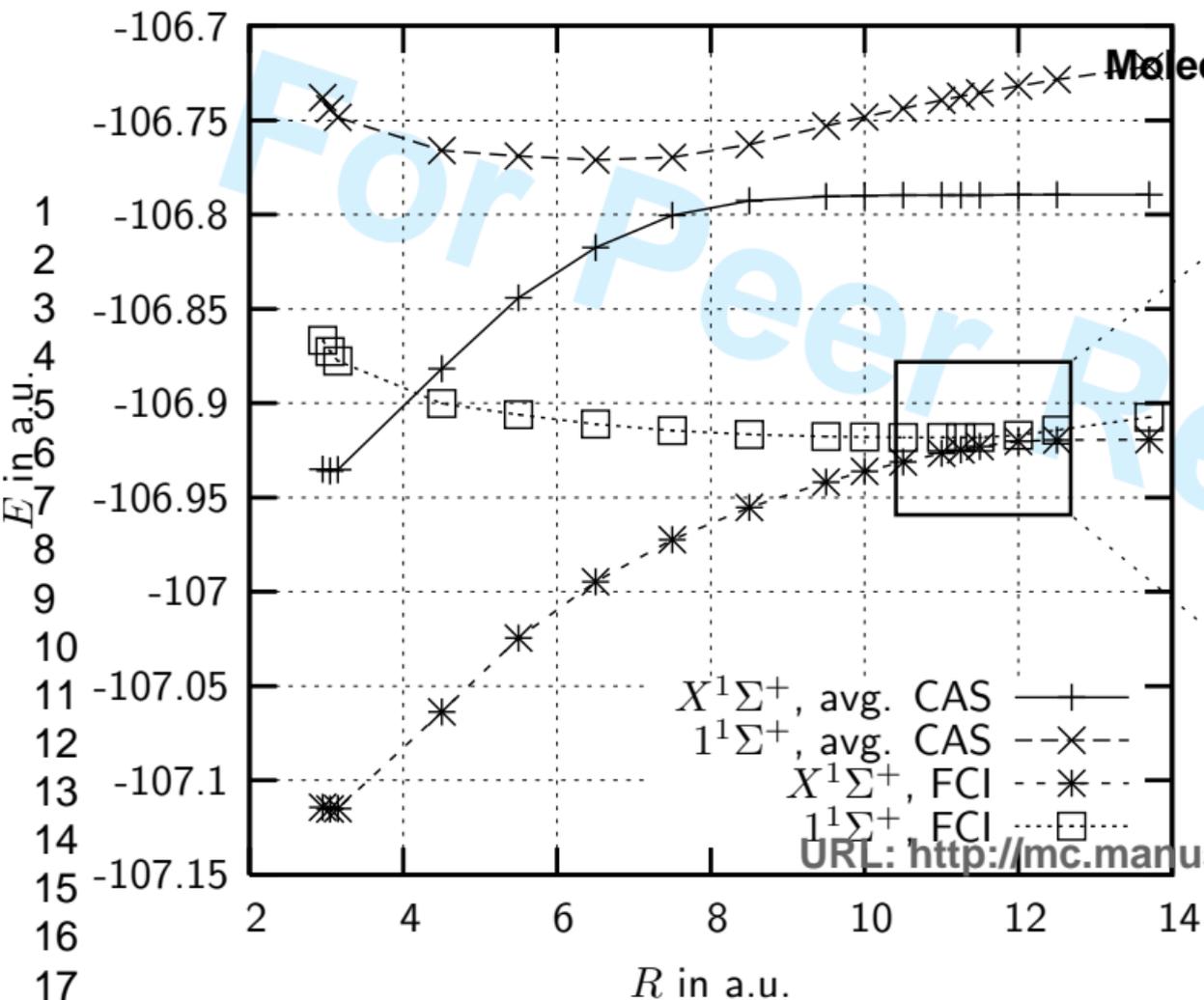
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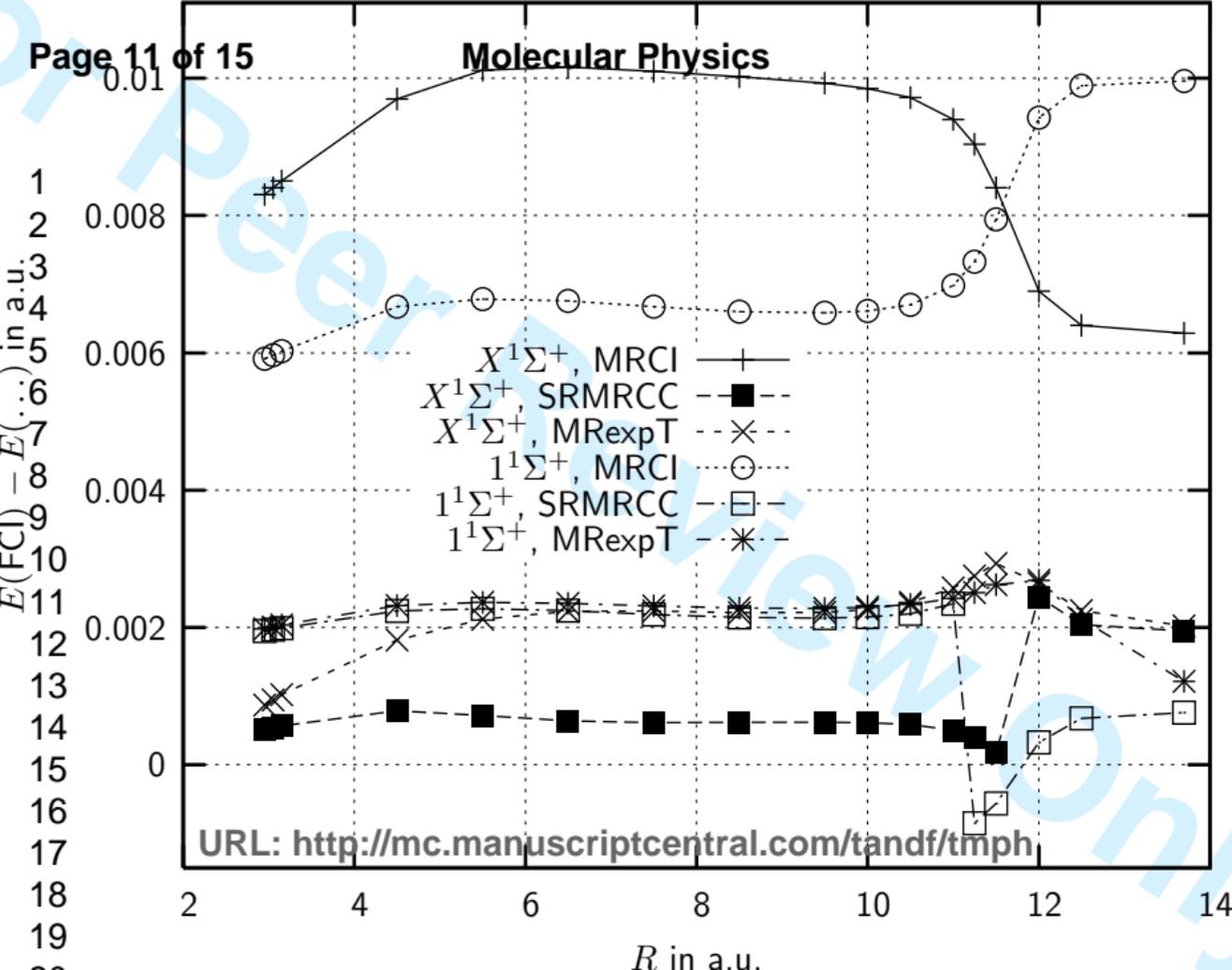
nuclear developments in coupled cluster methods" (INT 08-2A) program.

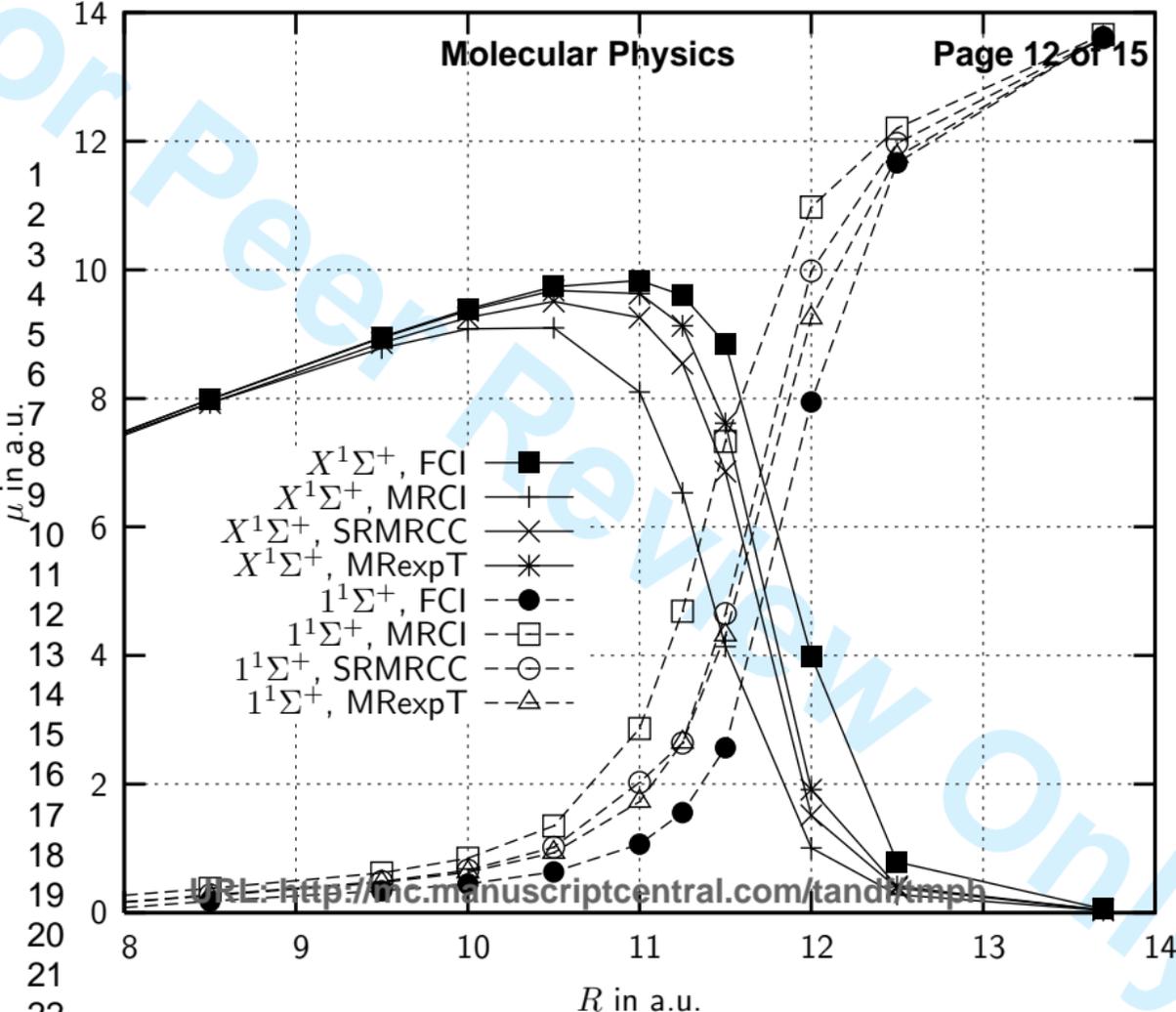
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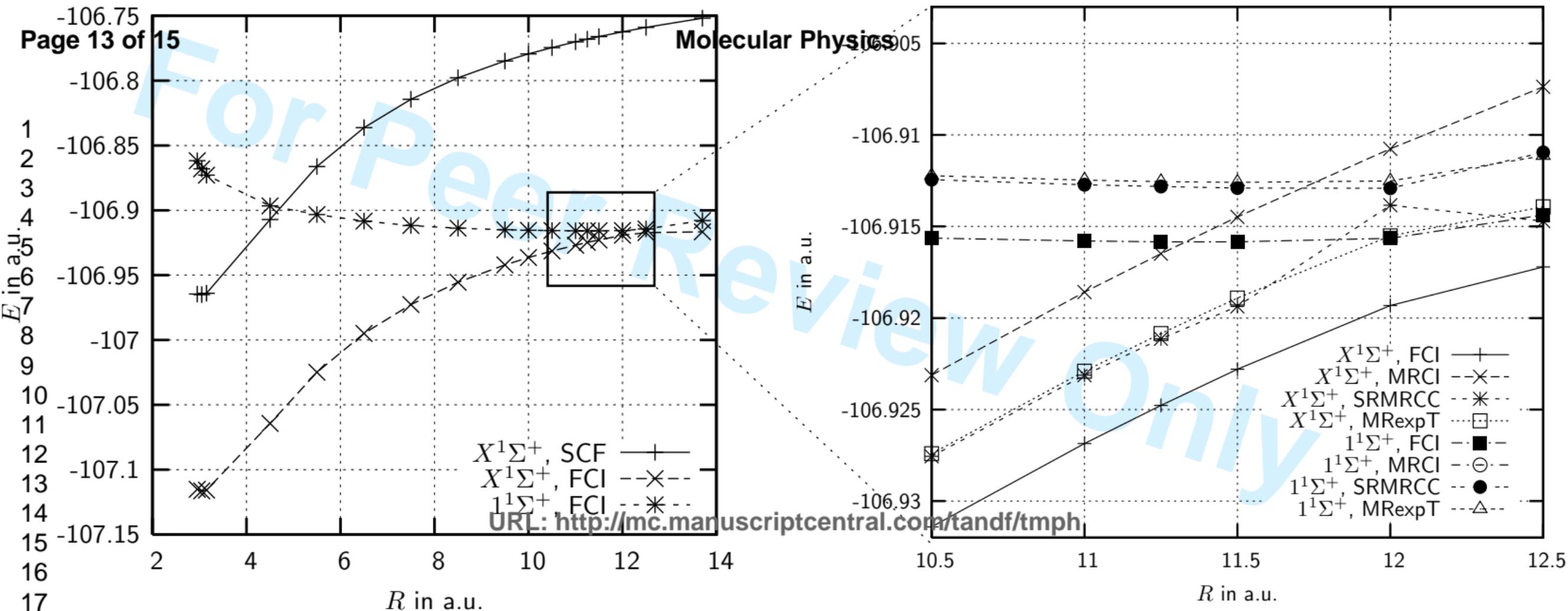
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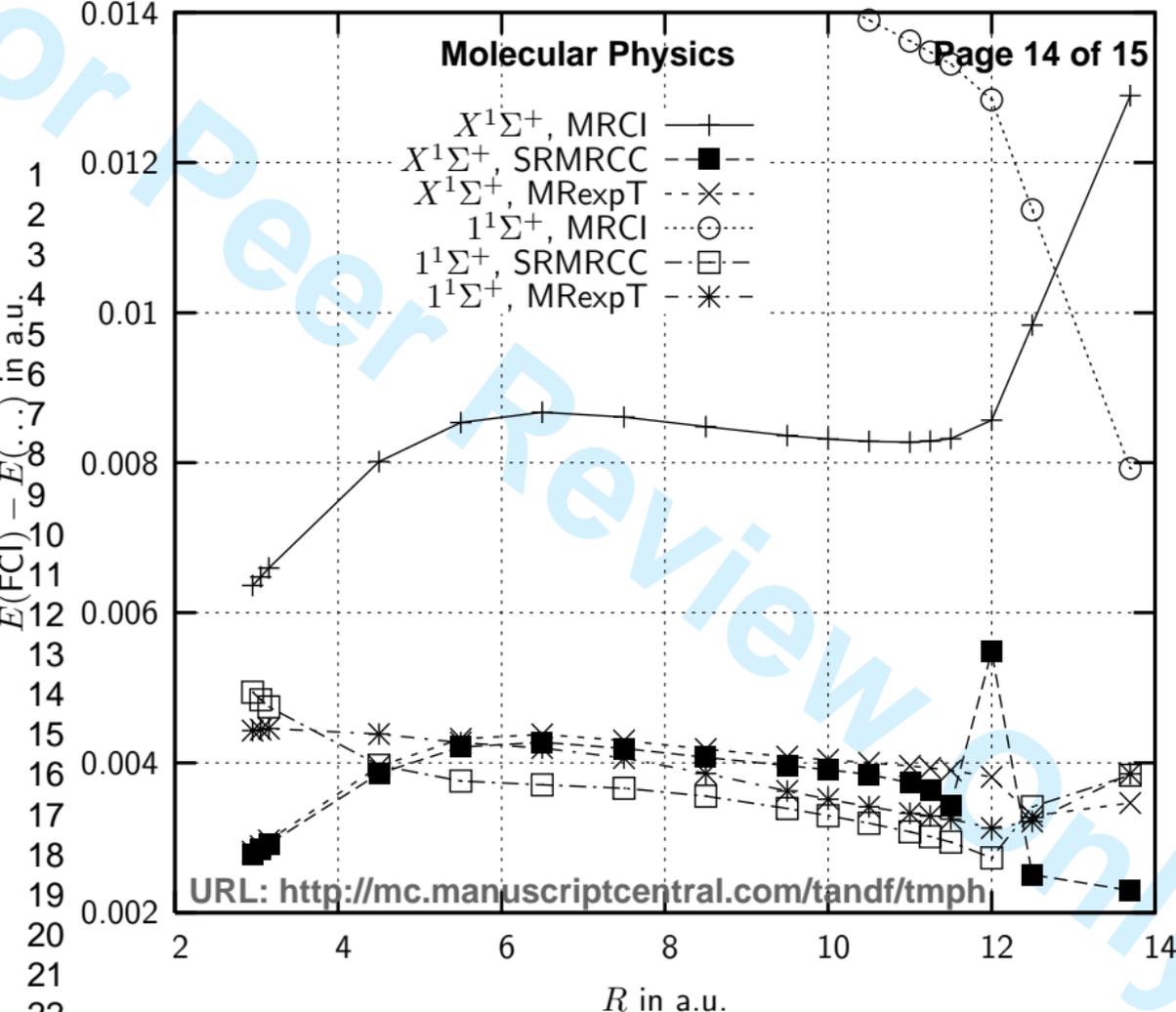
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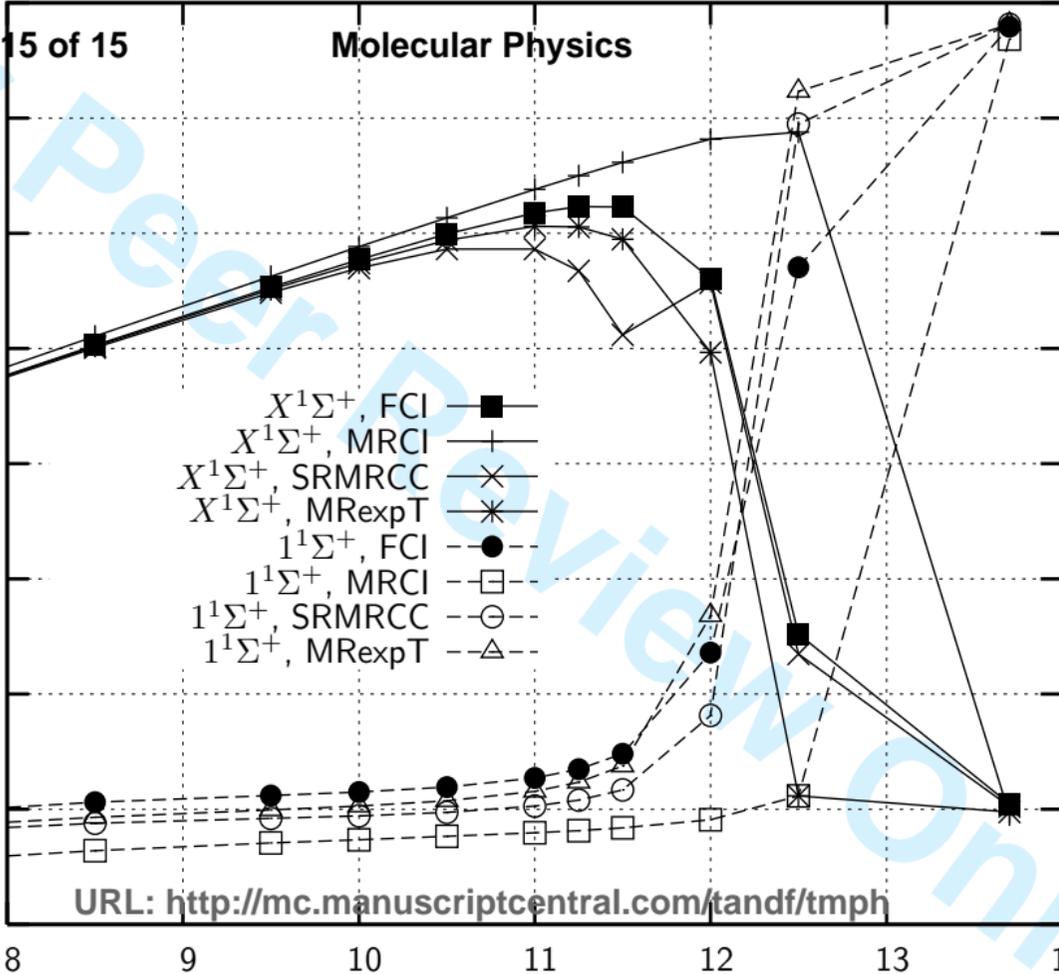








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