

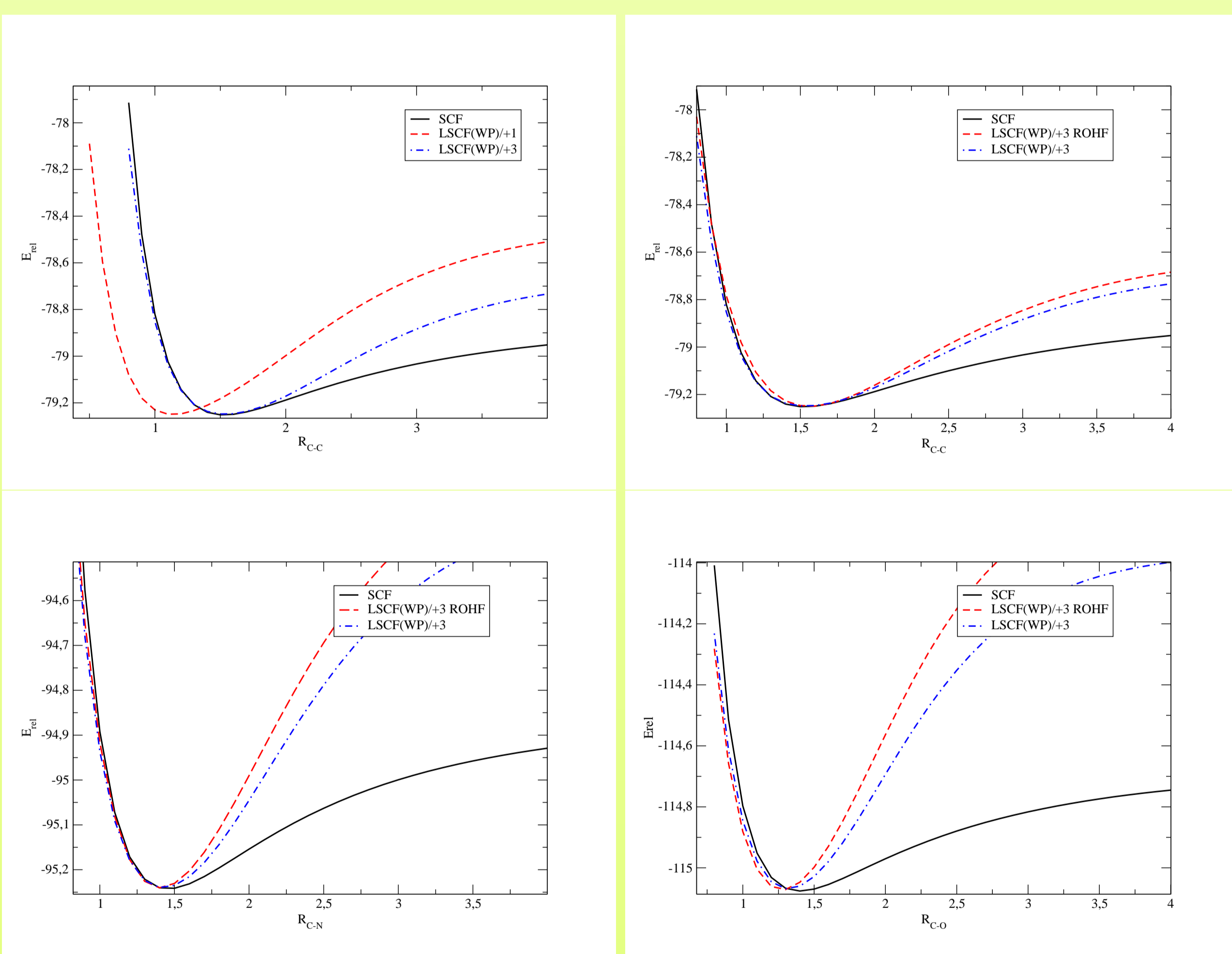
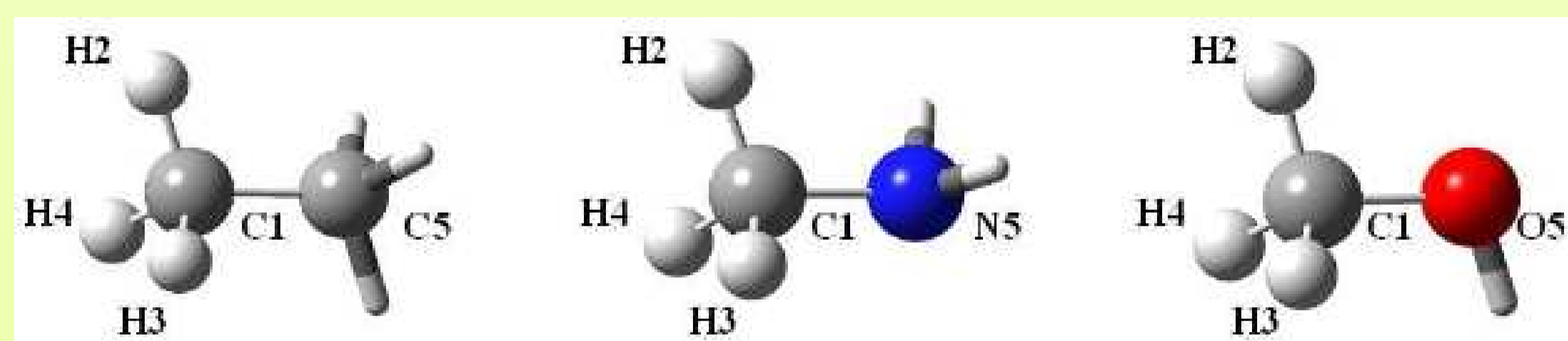
INTRODUCTION

The use of QM/MM methods to study chemical and biochemical processes is now well established. In the Local-SCF/MM framework [1, 2, 3], the dangling bond problem is circumvented by using a frozen bond orbital located between the two frontier atoms. To ensure the electroneutrality of the whole system, a charge of +1 is added to the classical point charge of the MM frontier atom as it contributes for one electron to the QM subsystem. This dual behaviour of the frontier atoms imposes to define a five-parameters bond potential to correctly describe the geometrical and energetic properties of the QM/MM boundary [2]. In a recent study [3], we proposed to use frozen core orbitals (FCOs) at the frontier atom as an alternative to the specific frontier bond potential in the LSCF/MM method. The charge carried by the frontier atom is then +3. The calculations illustrate that frontier bond length is correctly recovered without adding any specific force field potential. Hence, the general application of the method is enhanced since no extra parameters are needed. Here, we show that these core orbitals do not need to be frozen.

LSCF/MM METHODOLOGY WITH FRONTIER BOND POTENTIAL

- Old LSCF/MM Methodology [1]
 - Optimization of the wavefunction under the constraint that some MOs are kept frozen.
 - Use of *Strictly Localized Bond Orbitals* (SLBOs) to describe the QM/MM frontier.
 - Pseudo nuclear charge of +1 for the frontier atoms.
 - Five-parameters frontier bond potential [2] : $E_{XY} = (A + Br + Cr^2) e^{Dr} + \frac{E}{r}$
- New LSCF/MM Methodology [3]
 - Optimization of the wavefunction under the constraint that some MOs are kept frozen.
 - Use of *Strictly Localized Bond Orbitals* (SLBOs) to describe the QM/MM frontier.
 - Frozen/non frozen core orbital on the frontier atoms.
 - Pseudo nuclear charge of +3 for the frontier atoms.

TEST CALCULATIONS ON TARGET MOLECULES [4]



SECOND ROW ELEMENTS

Molecules	HF	LSCF(WP)/+1	LSCF(WP)/+3	LSCF(WP)/+3 ROHF
Ethane				
d(C1-C5)	1.527	1.138(-0.389)	1.565(0.038)	1.538(0.011)
d(C1-H2)	1.086	1.101(0.015)	1.092(0.006)	1.092(0.006)
a(H2-C1-C5)	111.2	113.9(2.7)	114.1(2.9)	114.7(3.5)
a(H2-C1-H3)	107.7	104.8(-2.9)	104.3(-3.4)	103.9(-3.8)
Methylamine				
d(C1-N5)	1.454	1.044(-0.410)	1.411(-0.043)	1.425(-0.029)
d(C1-Hx)	1.088	1.107(0.019)	1.095(0.007)	1.094(0.006)
a(H2-C1-N5)	114.6	113.4(-1.2)	114.0(-0.6)	114.3(-0.3)
a(H3-C1-N5)	109.4	115.6(6.2)	115.3(5.9)	115.3(5.9)
a(H2-C1-H3)	108.0	103.8(-4.2)	103.9(-4.1)	103.7(-4.3)
a(H3-C1-H4)	107.3	103.8(-3.5)	104.6(-2.7)	104.1(-3.2)
Methanol				
d(C1-O5)	1.399	0.957(-0.442)	1.280(-0.119)	1.322(-0.077)
d(C1-Hx)	1.085	1.112(0.027)	1.099(0.014)	1.096(0.011)
a(H2-C1-O5)	107.4	114.0(6.6)	113.3(5.9)	112.4(5.0)
a(H3-C1-O5)	112.0	117.0(5.0)	116.0(4.0)	116.8(4.8)
a(H2-C1-H3)	108.3	103.2(-5.1)	103.4(-4.9)	104.7(-3.6)
a(H3-C1-H4)	108.7	103.1(-5.6)	103.2(-5.5)	104.0(-4.7)

BASIS SET EFFECT

Ethane	d(C1-C5)		
	HF	LSCF(WP)/+3	Δ
STO-3G	1.538	1.585	0.048
3-21G	1.542	1.723	0.181
6-31G*	1.527	1.693	0.166
6-31G**	1.526	1.690	0.163
6-311G**	1.527	1.562	0.035
6-311++G**	1.527	1.584	0.058

THIRD ROW ELEMENTS

Molecules	HF	LSCF(WP)/+3	LSCF(WP)/+11
Silicon			
d(C-Si) 6-31G*	1.888	2.000(0.111)	2.011(0.123)
6-31G*+LANL2DZ	1.899	1.968(0.069)	2.122(0.223)
6-311G**	1.882	1.875(-0.007)	2.134(0.251)
Phosphorus			
d(C-P) 6-31G*	1.860	1.932(0.072)	1.892(0.032)
6-31G*+LANL2DZ	1.894	1.933(0.039)	2.032(0.138)
6-311G**	1.857	1.813(-0.045)	2.080(0.223)
Sulfur			
d(C-S) 6-31G*	1.817	1.855(0.038)	1.775(-0.042)
6-31G*+LANL2DZ	1.861	1.862(0.001)	1.873(0.012)
6-311G**	1.819	1.744(-0.075)	1.995(0.177)

CONCLUSION

The calculations illustrate that frontier bond length is correctly recovered without adding any specific force field potential. Hence, the general application of the method is enhanced since no extra parameters are needed. Here, we show that these core orbitals do not need to be frozen. Illustrative calculations prove that the same accuracy, as the one obtained with frozen core orbitals, can be reached for bond length between atoms of the second or third row of the periodic classification.

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