

# A Density Functional Theory for Symmetric Radical Cations

## From Bonding to Dissociation

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### Introduction

It is known for quite some time that approximate density functional (ADF) theories fail disastrously when describing the dissociative symmetric radical

cations  $R_2^+$ . Considering this dissociation limit, previous work has shown that Hartree-Fock (HF) theory favors the  $R^{+1}$ - $R^0$  charge distribution while DF approximations favor the  $R^{+0.5}$ - $R^{+0.5}$ . Yet, general quantum mechanical principles indicate that both these (as well as all intermediate) average charge distributions are asymptotically energy degenerate.

Thus HF and ADF theories mistakenly break the symmetry but in a contradicting way. In this work we show how to construct system-dependent long-range corrected (LC) density functionals that can successfully treat this class of molecules, avoiding the spurious symmetry breaking. Examples and comparisons to experimental data is given. It is shown that the new LC theory improves considerably the theoretical description of the bond properties, the long-range form of the asymptotic potential curve as well as the atomic polarizability.

As well we will show an exact representation of the exchange-correlation energy within DFT which spawns a class of approximations leading to correct long-range asymptotic behavior

### Method

#### DFT in General

We consider a system of  $N$  electrons, with the Hamiltonian:

$$\hat{H} = \hat{T} + \hat{V} + \hat{U}$$

Where  $\hat{T} = \sum_{i=1}^N \left( -\frac{1}{2} \nabla_i^2 \right)$ , is the kinetic energy,  $\hat{V} = \sum_{i=1}^N v(\hat{r}_i)$ , is the external potential, and  $\hat{U} = \frac{1}{2} \sum_{i,j=1}^N u(\hat{r}_i, \hat{r}_j)$  is the interaction, with  $u(r)$ :

$$u(r) = \frac{1}{r}$$

In DFT all expectation values are functionals of the ground state density  $n(r)$ . The energy functional:

$$E_{v,N}[n] = T_s[n] + V[n] + E_n[n] + E_{xc}[n]$$

$T_s[n]$  is the noninteracting kinetic energy,

$$V[n] = \frac{1}{2} \int v(r) n(r) d^3r$$

$$E_n[n] = \frac{1}{2} \int n(r) n(r') u(|r-r'|) d^3r d^3r'$$

The  $E_{xc}$  is of course practically impossible to determine exactly

### Approach

The range separated hybrid addresses the problem of self-repulsion in DFT and TDDFT while maintaining reasonable performance for the traditional properties. It is based on a range separation of the e-e coulomb potential

$$\frac{1}{r} = \frac{1 - \text{erf}(\gamma r)}{r} + \frac{\text{erf}(\gamma r)}{r}$$

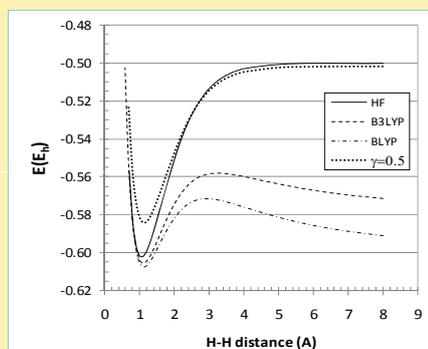
implemented in the exchange functional. is the range separation parameter. The first part, short-range exchange, is described by a local functional and the second, long-range exchange, is treated as an explicit exchange term.

### System – independent $\gamma$

In previous work we developed a functional with system-independent parameter  $\gamma=0.5$ , the functional will be denoted here as BNL functional.

### Results

The potential curves of  $H_2^+$  in a cc-pVTZ basis using different theories. The “HF” theory is the exact variational solution in this case.



### System - dependent $\gamma$

In this work the  $\gamma$  parameter is system-dependent and should ensure an exact condition:

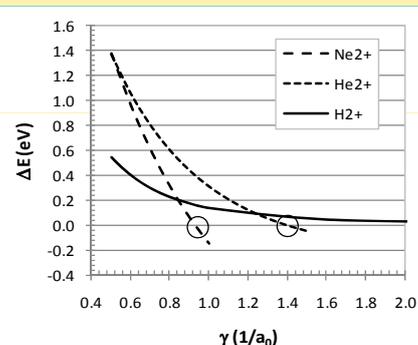
$$\Delta E(\mathbf{r}_0) = E\left(\mathbf{r}_0, \frac{1}{2}\right) - E(\mathbf{r}_0, 1) = 0$$

Here  $r_0=20\text{\AA}$ ,  $E\left(\mathbf{r}_0, \frac{1}{2}\right)$  is energy of system with symmetric charge distribution and  $E(\mathbf{r}_0, 1)$  is energy for system with integer average charge distribution.

BNL with the proper LC parameter  $\gamma^*$  will be denoted henceforth BNL\*.

### Results

The dependence of the localization-delocalization energy difference on the value of the parameter  $\gamma$  in the LC functional



Data for  $R_2^+$ ,  $R=H, He$  and  $Ne$  calculated in the cc-pVTZ basis. All energies in kcal/mole.

Property	R	BLYP	B3LYP	HF	BNL	BNL*	Exp.
Enthalpy by atomization	H	66	65	60.9	60.9	60.9	61
	He	82	75	43	74	59	55
	Ne	75	60	2	59	34	32
Enthalpy by asymptote	H	NA	NA	60.9	50	60.9	61
	He	NA	NA	43	47	59	55
	Ne	NA	NA	2	27	34	32
$r_{opt}$	H	1.1	1.1	1.06	1.2	1.06	1.05
	He	1.2	1.1	1.075	1.2	1.078	1.080
	Ne	1.9	1.9	1.7	1.760	1.72	1.765
$h\omega/2$	H	2.7	2.9	3.3	2.9	3.3	3.32
	He	1.7	2.0	2.5	2.1	2.5	2.42
	Ne	0.5	0.6	0.9	0.726	0.8	0.729
$\gamma_{opt} / \gamma_{opt}$	H	NA	NA	1	0.6	1	1
	He	NA	NA	0.98	NA	0.98	1
	Ne	NA	NA	1.01	NA	1.02	1
$\alpha_R^{asymp}(\alpha_0^5)$	H	5.3	5.6	4.51	5.8	4.51	4.50
	He	1.6	1.5	1.34	1.8	1.41	1.38
	Ne	3.1	2.9	2.4	3.2	2.70	2.66

Here Enthalpy by atomization calculated by:

$E_{at} - E(r_{opt}) + \frac{1}{2} h\omega$ , then  $E_{at} = E_R + E_{R^+}$ , and Enthalpy by asymptote calculated by:  $E_{\infty} - E(r_{opt}) + \frac{1}{2} h\omega$ .  $\alpha_R$  is an atomic polarizability and  $\alpha_{LC} = \lim_{r \rightarrow \infty} E(r) r^2 / 2$

### Discussion

The broader impact of these findings is that the parameter must not be considered a system-independent quantity. It seems that for universality to be achieved,  $\gamma$  must be system specific and techniques for its ab initio determination from the calculation itself, as done here, need to be developed. This approach can perhaps be made into a general strategy so that before any system is calculated, the parameter can be determined by the above procedure for  $R_2^+$ . This will in effect serve to impose the linear energy dependence on the fractional particle number as determined by Perdew et al. exhibiting both derivative discontinuity and correct long-range behavior