Partition Density Functional Theory

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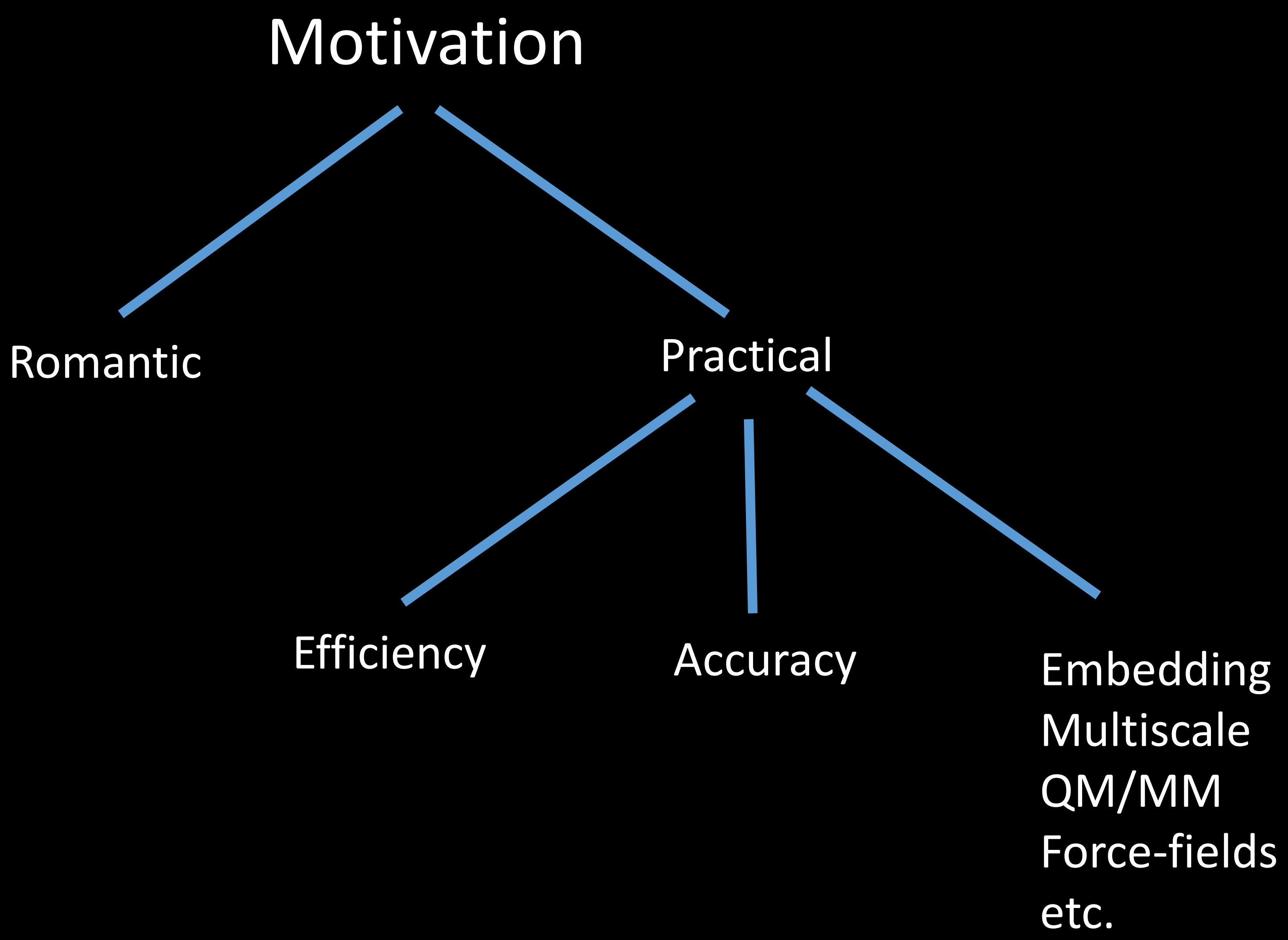
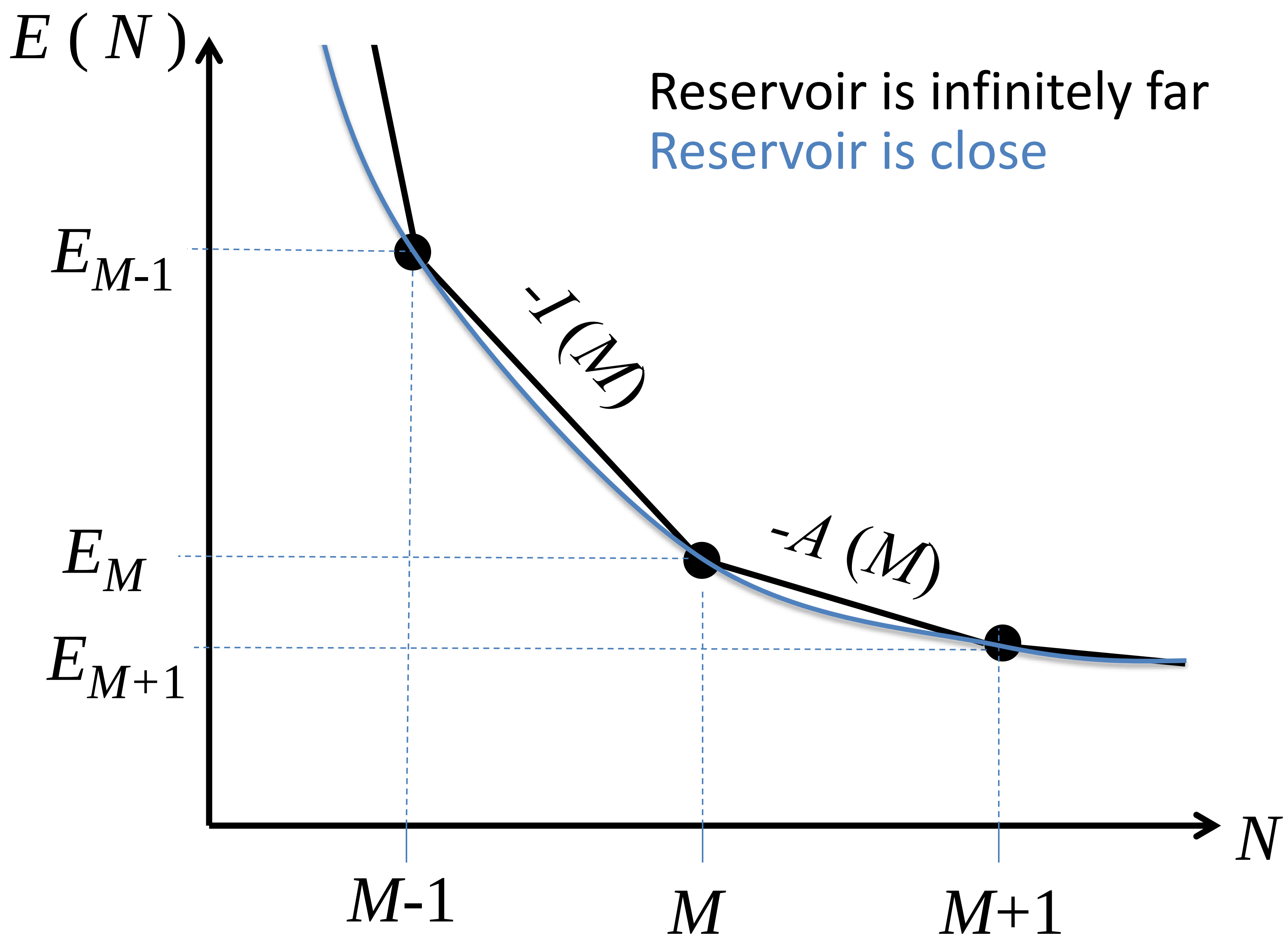
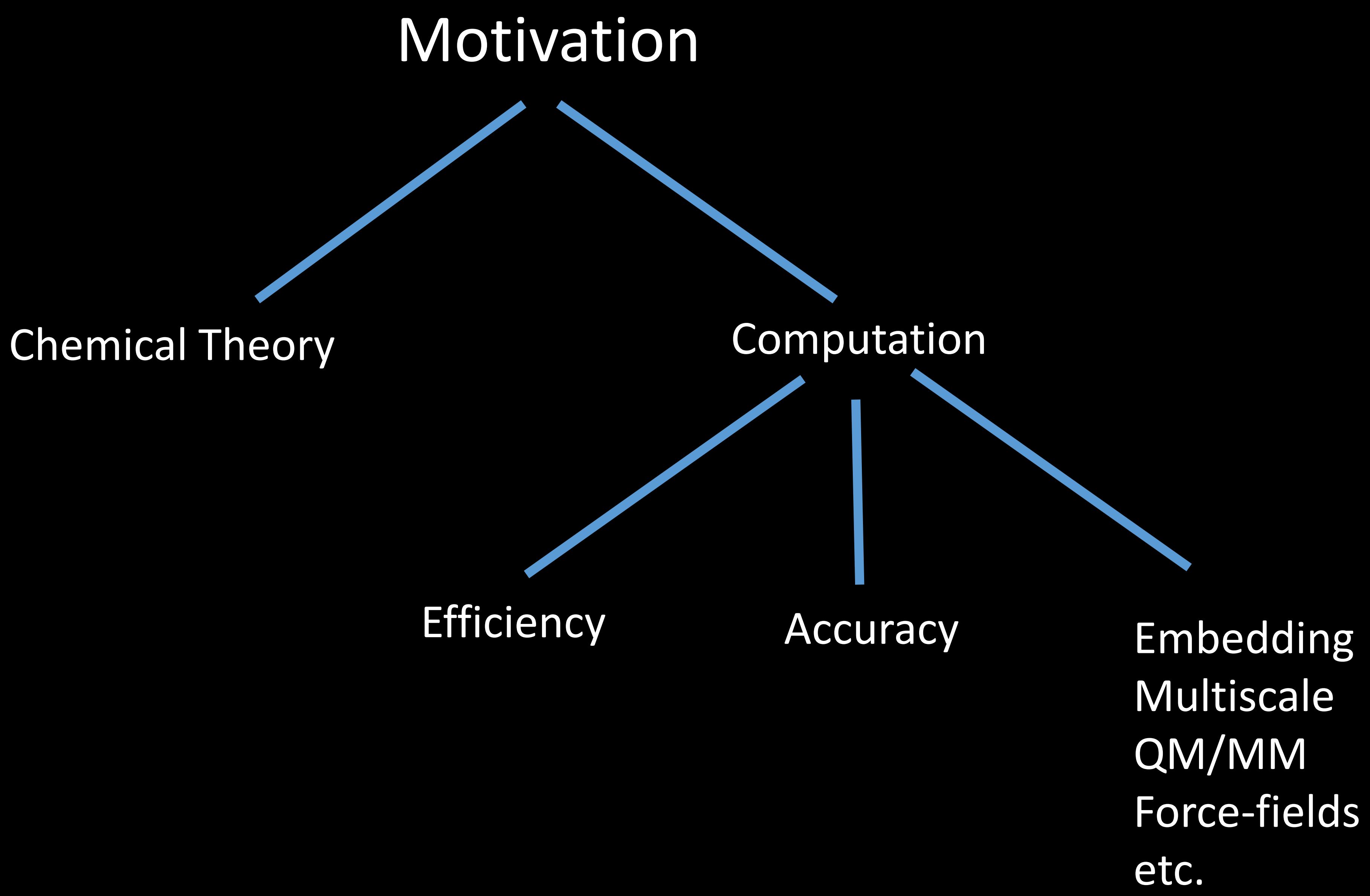
Outline

1. Motivation
2. Partition potential theorem
3. Partition-DFT
4. Fixing errors of approximate functionals with Partition-DFT


Motivation
Romantic
Practical
Efficiency
Accuracy
Embedding
Multiscale
QM/MM
Force-fields
etc.


E (N)
Reservoir is infinitely far
Reservoir is close
E_{M-1}
-I (M)
-A (M)
E_M
E_{M+1}
M-1
M
M+1
N


Motivation
Chemical Theory
Computation
Efficiency
Accuracy
Embedding
Multiscale
QM/MM
Force-fields
etc.

Partition Potential Theorem

$$v(\mathbf{r}) = \sum_\alpha v_\alpha(\mathbf{r})$$

$\updownarrow N$

$$\sum_\alpha n_\alpha(\mathbf{r}) = n(\mathbf{r})$$

$\updownarrow N_\alpha$

$$v_\alpha(\mathbf{r}) + v_p(\mathbf{r})$$

For a given set of fragment occupation numbers $\{ N_\alpha \}$ there is at most one potential $v_p(\mathbf{r})$ and set of densities $\{n_\alpha(\mathbf{r})\}$ such that each $n_\alpha(\mathbf{r})$ is the ensemble ground-state density of N_α electrons in $v_\alpha(\mathbf{r})$ + $v_p(\mathbf{r})$.

M.H. Cohen and A. Wasserman, J. Stat. Phys. **125**, 1121 (2006).

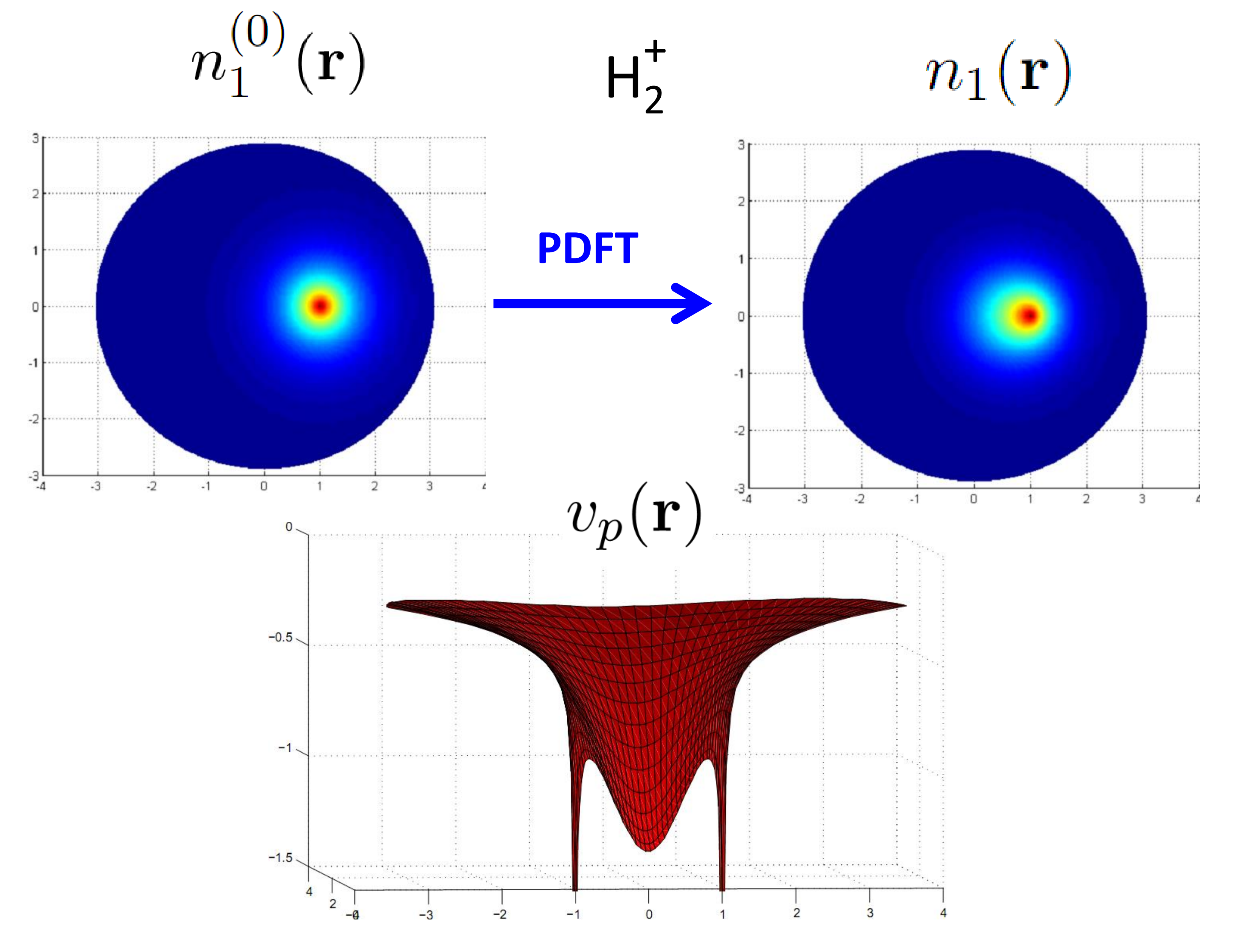
Proof of PPT (2 fragments, integer numbers)

$$v(\mathbf{r}) = v_1(\mathbf{r}) + v_2(\mathbf{r})$$

$$v_p(\mathbf{r}) \longrightarrow \{n_1(\mathbf{r}), n_2(\mathbf{r})\} \qquad v'_p(\mathbf{r}) \longrightarrow \{n'_1(\mathbf{r}), n'_2(\mathbf{r})\}$$

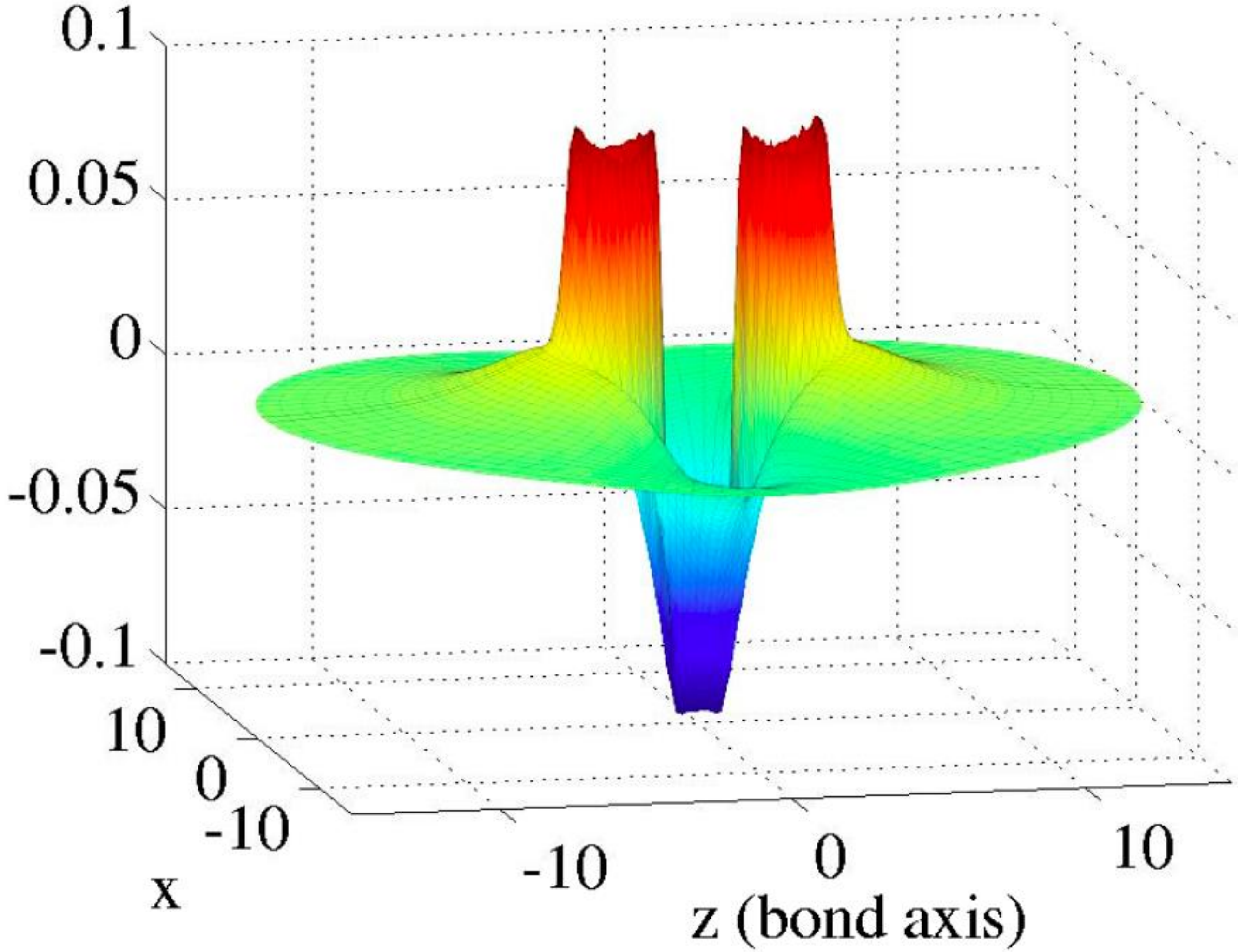
$$n_1(\mathbf{r}) + n_2(\mathbf{r}) = n(\mathbf{r}) \qquad n'_1(\mathbf{r}) + n'_2(\mathbf{r}) = n(\mathbf{r})$$

$$\begin{aligned}
E_f[\mathbf{n}] &= F[n_1] + \int d\mathbf{r}\,(v_1(\mathbf{r}) + v_p(\mathbf{r}))\,n_1(\mathbf{r}) + F[n_2] + \int d\mathbf{r}\,(v_2(\mathbf{r}) + v_p(\mathbf{r}))\,n_2(\mathbf{r}) \\
&= E[n_1] + E[n_2] + \int d\mathbf{r} v_p(\mathbf{r}) n(\mathbf{r}) \\
&< F[n'_1] + \int d\mathbf{r}\,(v_1(\mathbf{r}) + v_p(\mathbf{r}))\,n'_1(\mathbf{r}) + F[n'_2] + \int d\mathbf{r}\,(v_2(\mathbf{r}) + v_p(\mathbf{r}))\,n'_2(\mathbf{r}) \\
&= E[n'_1] + E[n'_2] + \int d\mathbf{r} v_p(\mathbf{r}) n(\mathbf{r})
\end{aligned}$$



$n_1^{(0)}(\mathbf{r})$
H_2^+
$n_1(\mathbf{r})$
PDFT
$v_p(\mathbf{r})$

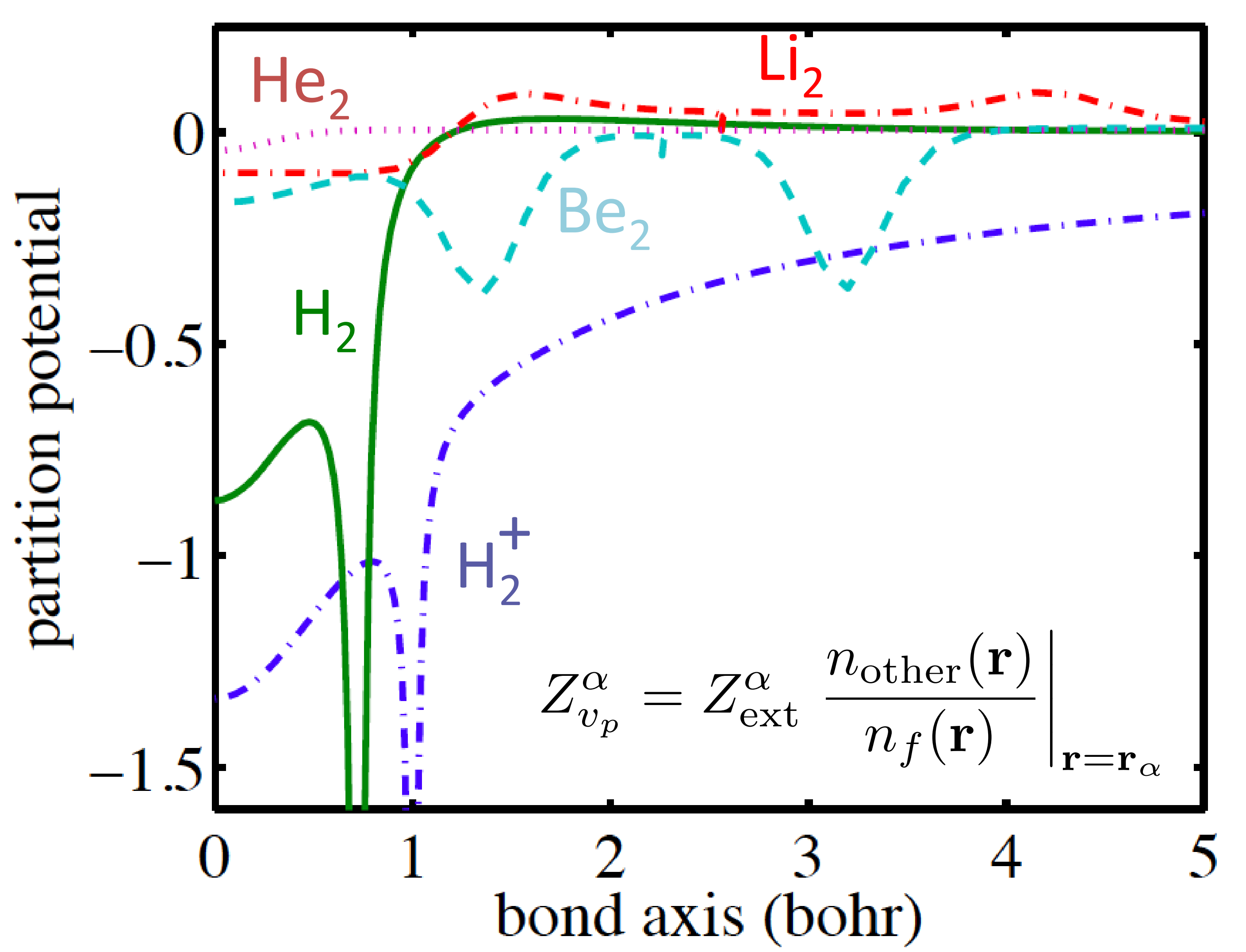
Partition potential – Li_2



CADMium:
500 to 14,000 points
Area ~ 300 a.u.^{2}

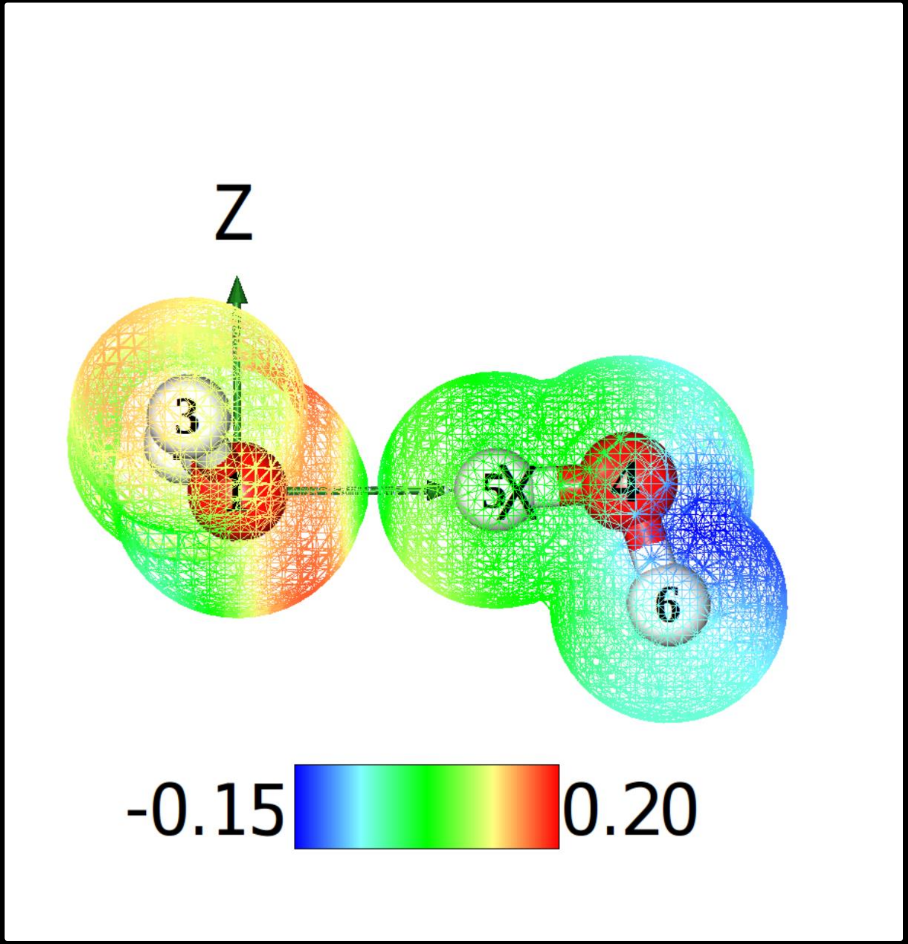
J. Nafziger and A. Wasserman, J. Phys. Chem. A **118**, 7623 (2014).

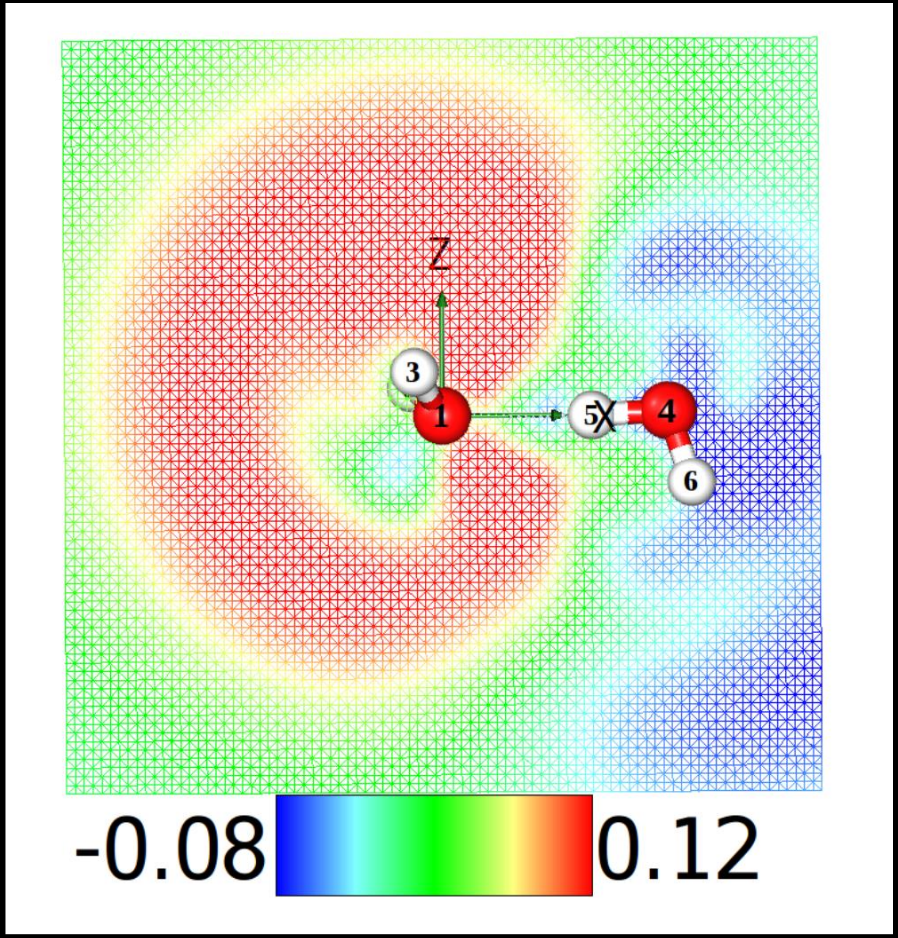
Partition potential along internuclear axis



J. Nafziger and A. Wasserman, J. Phys. Chem. A **118**, 7623 (2014).

Partition Potential – Water dimer

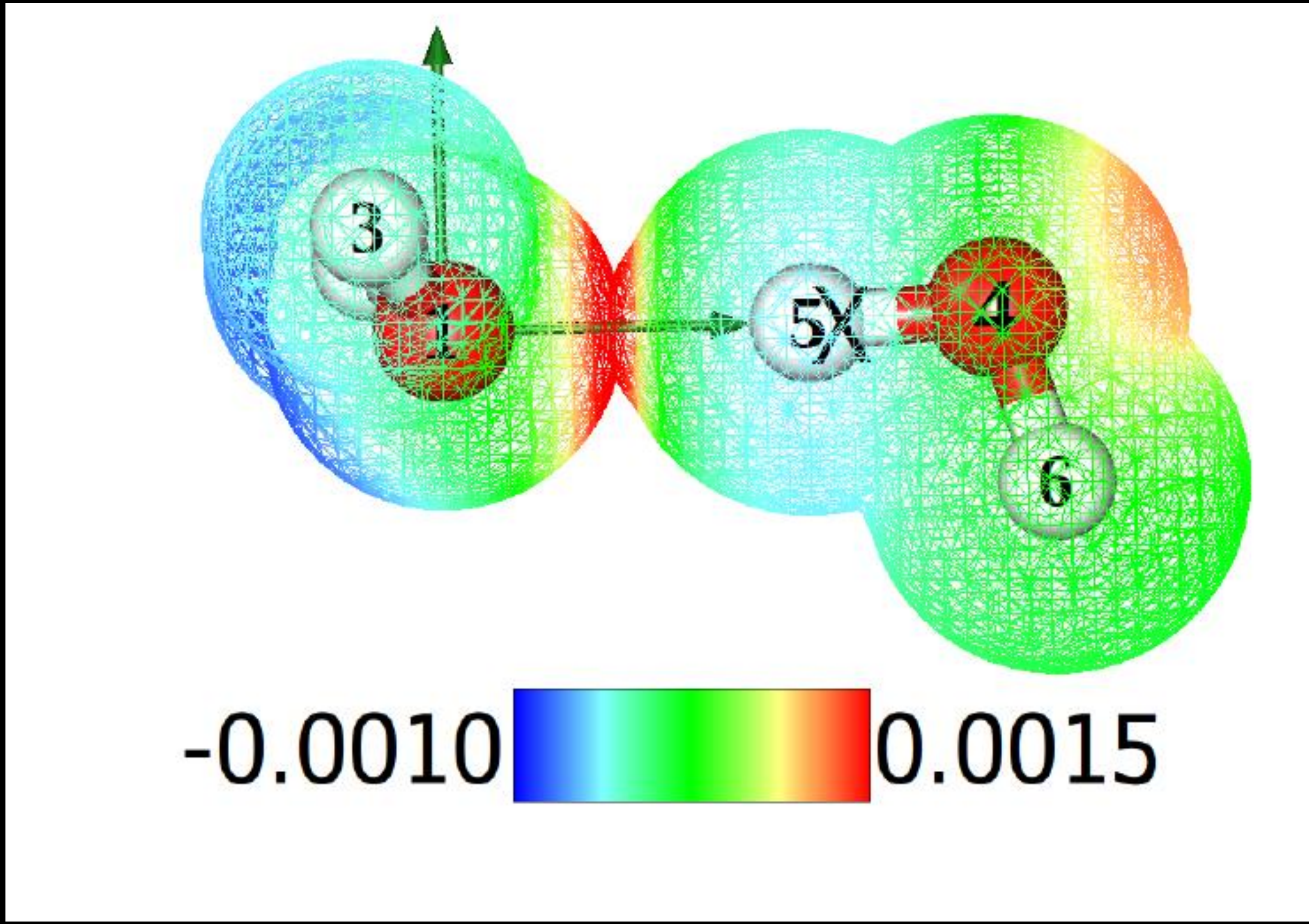




S. Gomez, J. Nafziger, A. Restrepo, and A. Wasserman, *in preparation*.

B3LYP / aug-cc-pvTz

Water dimer: Difference between actual density and sum of isolated monomer densities



S. Gomez, J. Nafziger, A. Restrepo, and A. Wasserman, *in preparation*.

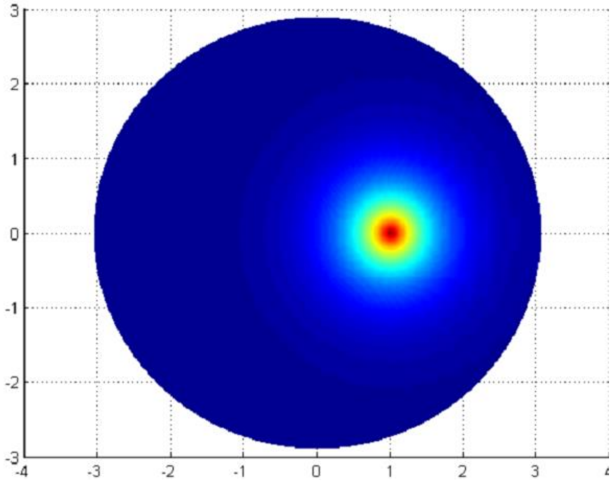
B3LYP / aug-cc-pvTz

Partition Density Functional Theory

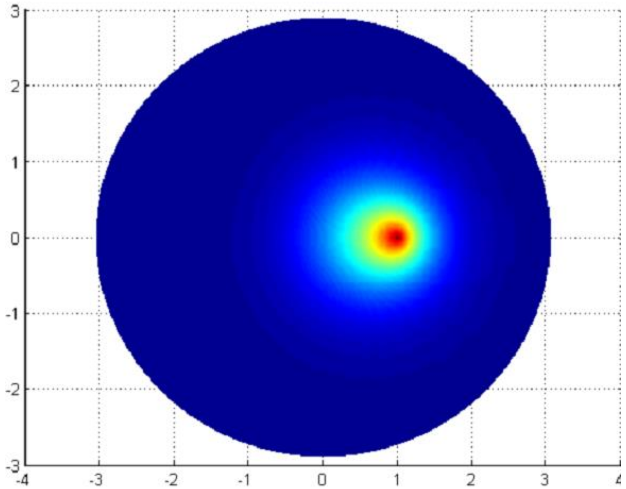
For given approximation to $E_{\mathrm{xc}}[n]$, *exactly* reproduces the results of a molecular DFT calculation.

P. Elliott, K. Burke, M.H. Cohen and A. Wasserman, Phys. Rev. A **82**, 024501 (2010).

$n_1^{(0)}(\mathbf{r})$ H_2^+ $n_1(\mathbf{r})$

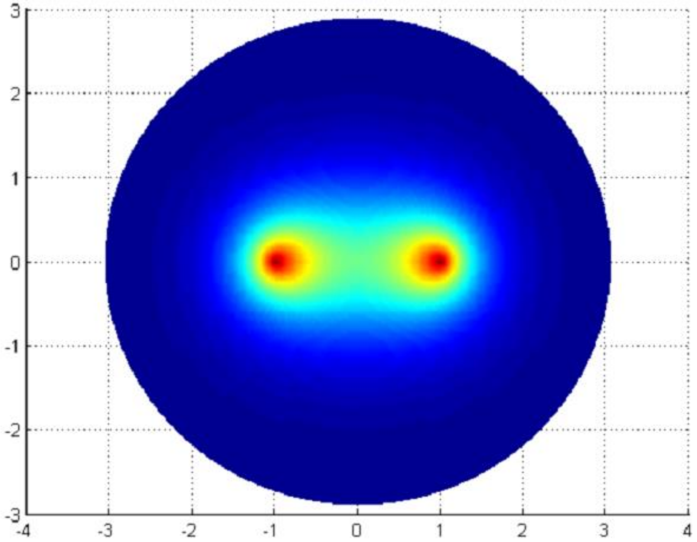


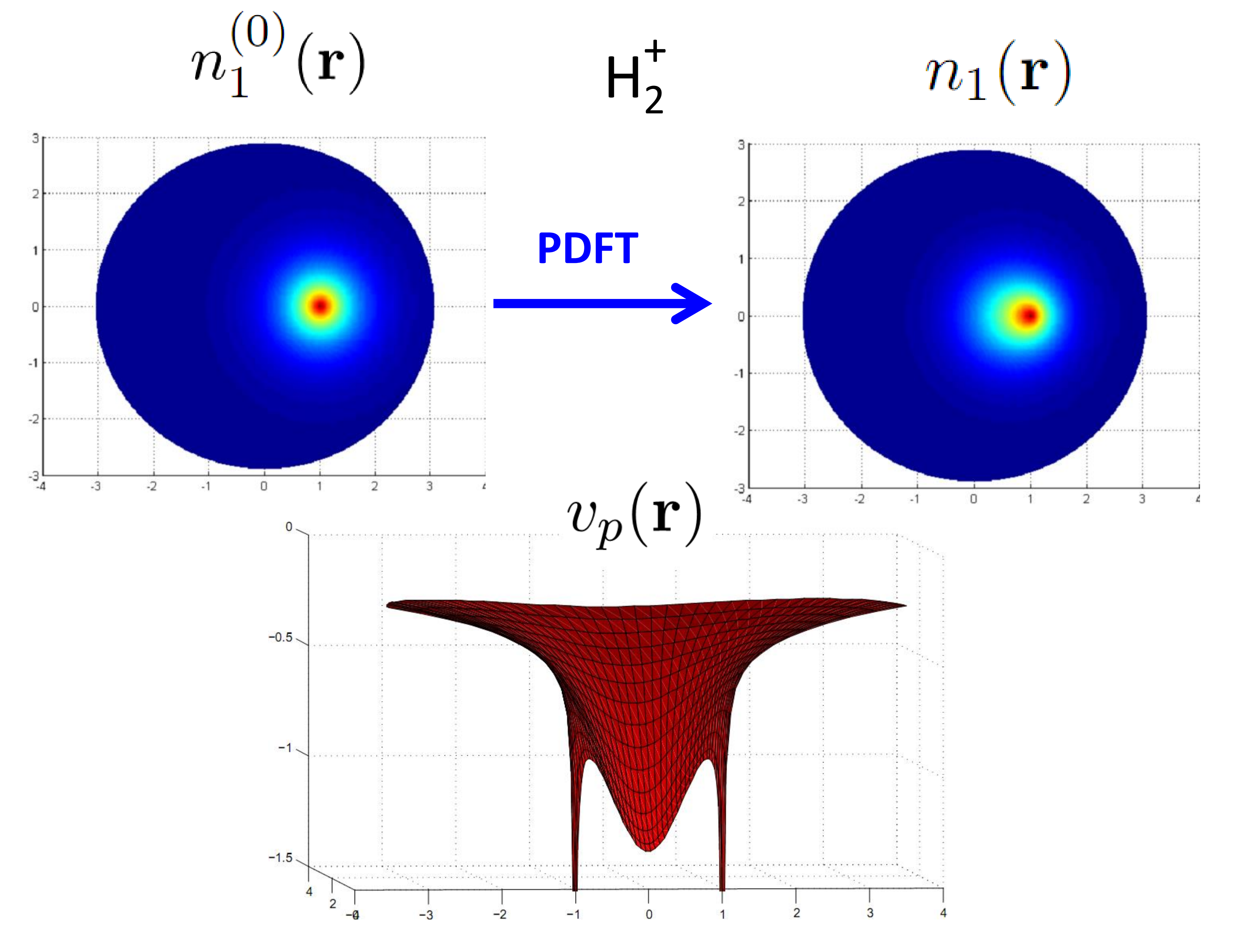
PDFT →



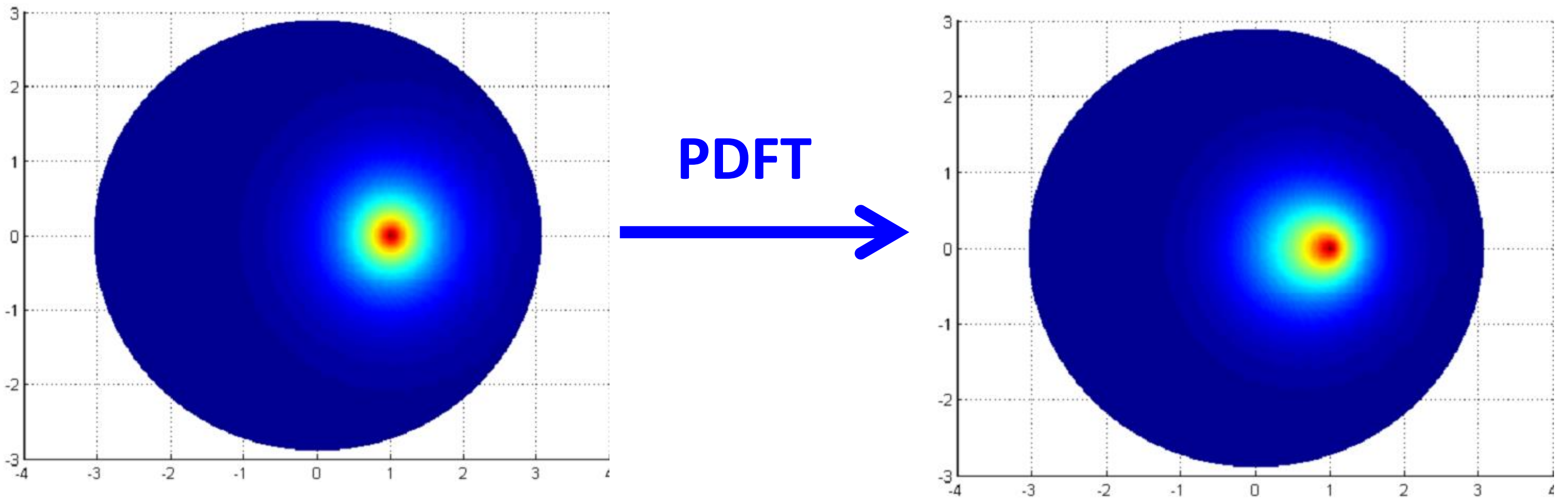
Exact molecular density

$$n(\mathbf{r}) = n_1(\mathbf{r}) + n_2(\mathbf{r})$$




$n_1^{(0)}(\mathbf{r})$
H_2^+
$n_1(\mathbf{r})$
PDFT
$v_p(\mathbf{r})$

$n_1^{(0)}(\mathbf{r})$ H_2^+ $n_1(\mathbf{r})$



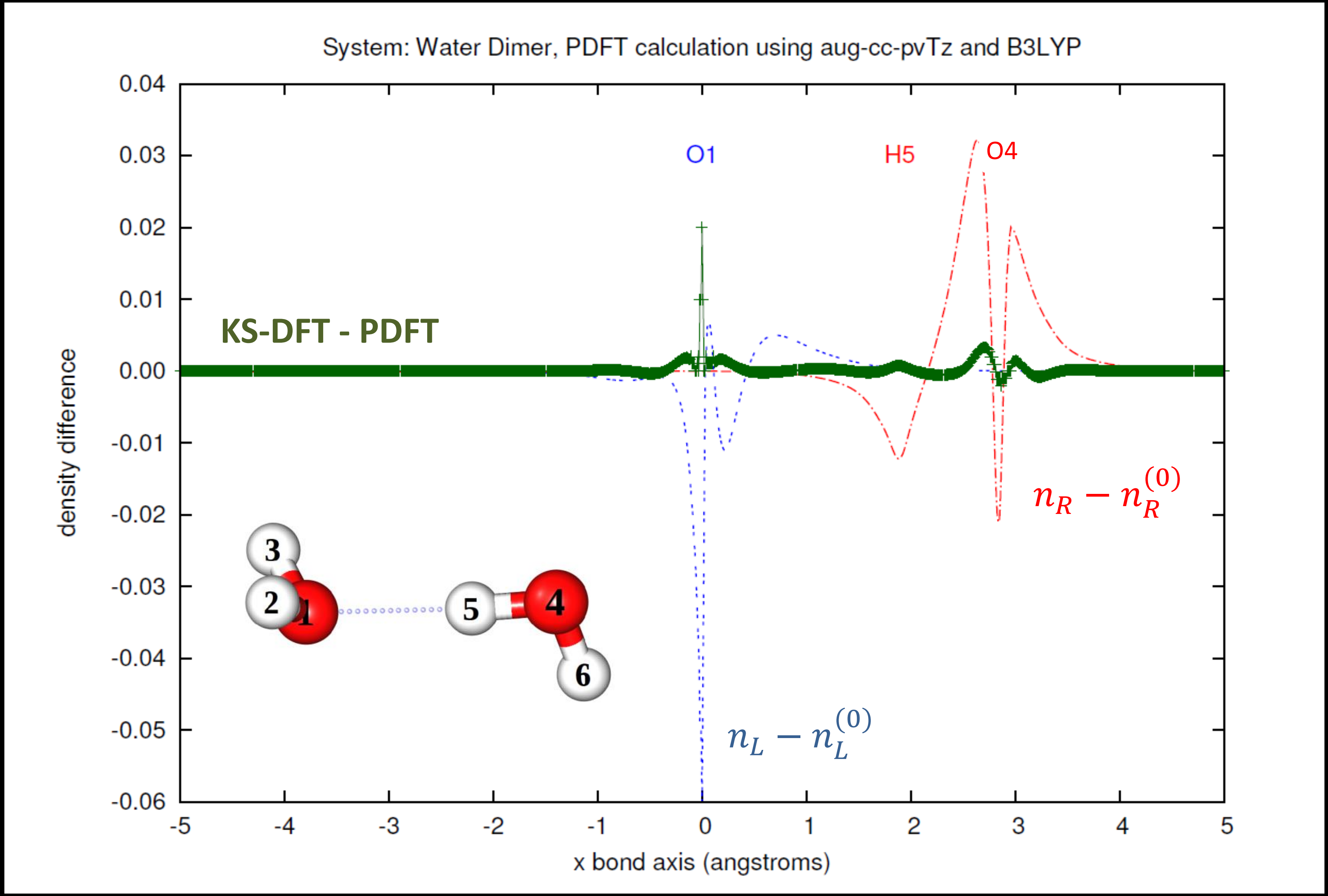
Molecular calculation: -1.10263421949(5) a.u.

PDFT calculation: -1.102634219497 a.u.

Comparison between molecular energies (a.u.) obtained from PDFT and from standard KS-DFT calculations using the same functional (B3LYP) and basis set (aug-cc-pvTz) for both.

	E(PDFT)	E(DFT)	Error
He_2 ($R = 0.5$)	−5.569777622113	−5.569777624227	−3.80E-10
He_2 ($R = 0.8$)	−5.709621657286	−5.709621657554	−4.69E-11
H_2 (OSH)	−1.180048619032	−1.180048623628	−3.89E-09
H_2 (CSH)	−1.180048619388	−1.180048623628	−3.59E-09

J. Nafziger, Q. Wu, and A. Wasserman, J. Chem. Phys. **135**, 234101 (2011).

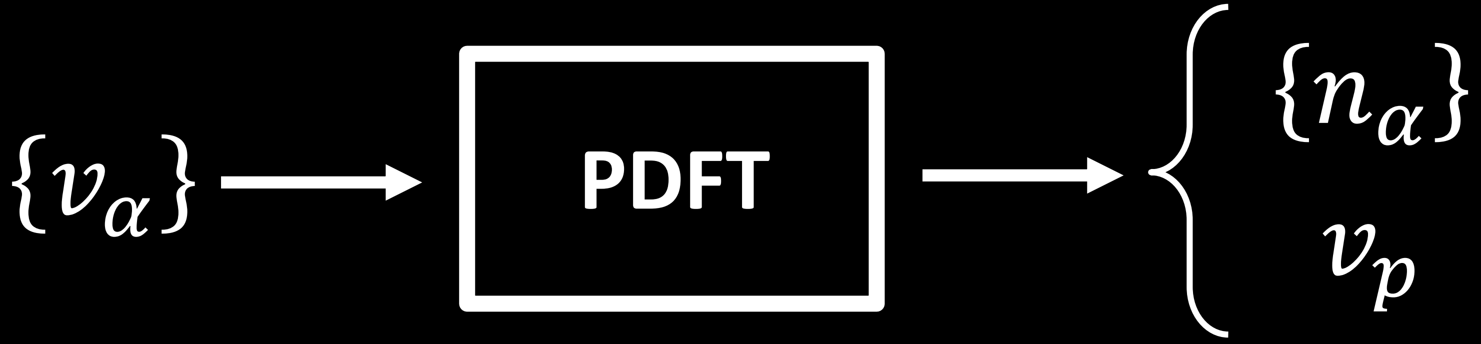


NWChem

S. Gomez, J. Nafziger, A. Restrepo, and A. Wasserman, *in preparation*.

B3LYP / aug-cc-pvTz

Partition Density Functional Theory



For given approximation to $E_{\mathrm{xc}}[n]$, *exactly* reproduces the results of a molecular DFT calculation.

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Partition Density Functional Theory

Constrained minimization of:

$$E_f[\{n_\alpha\}] \equiv \sum_\alpha E_\alpha[n_\alpha]$$

where:

$$E_\alpha[n_\alpha] = \nu_\alpha E_{v_\alpha}[n_{p_\alpha+1}] + (1-\nu_\alpha)E_{v_\alpha}[n_{p_\alpha}]$$

$$G[\{n_\alpha\}] = E_f[\{n_\alpha\}] + \int v_p(\mathbf{r})\,(n_f(\mathbf{r}) - n(\mathbf{r}))\,d\mathbf{r} - \mu_m\left(\int n_f(\mathbf{r})d\mathbf{r} - N\right)$$

M.H. Cohen and A. Wasserman, JPCA **111**, 2229 (2007).
P. Elliott, K. Burke, M.H. Cohen and A. Wasserman, Phys. Rev. A **82**, 024501 (2010).

Partition Density Functional Theory

$$v_{\rm nuc}(\mathbf{r}) = \sum_\alpha v^\alpha_{\rm nuc}(\mathbf{r})$$

Solve KS equations for each fragment ⟹ $\{n^0_\alpha(\mathbf{r})\}$

$$\sum_\alpha n^{(0)}_\alpha(\mathbf{r}) \equiv n^{(0)}(\mathbf{r})$$

Promolecule

Invert KS equations

For a given approximation to $E_{\rm xc}[n]$, this algorithm is exactly equivalent to solving the KS equations for N electrons in $v_{\rm nuc}(\mathbf{r})$.

$$v^{(0)}_{s,f,\alpha}(\mathbf{r}) = v_s[n^{(0)}_\alpha](\mathbf{r}) + \left\{v_{\rm nuc}(\mathbf{r}) + v_{\rm HXC}[n^{(0)}](\mathbf{r}) - v_s[n^{(0)}](\mathbf{r})\right\}$$

Effective KS fragment potential

Would be zero if promolecule density were the correct gs density

P. Elliott, K. Burke, M.H. Cohen and A. Wasserman, PRA **82**, 024501 (2010).

Partition Density Functional Theory

$$\left[-\frac{1}{2}\nabla^2 + v^{(0)}_{s,f,\alpha}(\mathbf{r})\right]\phi^{(1)}_j(\mathbf{r}) = \epsilon^{(1)}_j \phi^{(1)}_j(\mathbf{r})$$

$$\left\{n^{(1)}_\alpha(\mathbf{r})\right\} = \left\{\sum_{j=1}^{N^{(0)}_\alpha} |\phi^{(1)}_j(\mathbf{r})|^2\right\}$$ For all α

New promolecule: $$n^{(1)}(\mathbf{r}) = \sum_\alpha n^{(1)}_\alpha(\mathbf{r})$$

New effective KS potential for fragment α:

$$v^{(1)}_{s,f,\alpha}(\mathbf{r}) = v_s[n^{(1)}_\alpha](\mathbf{r}) + \left\{v_{\text{nuc}}(\mathbf{r}) + v_{\text{HXC}}[n^{(1)}](\mathbf{r}) - v_s[n^{(1)}](\mathbf{r})\right\}$$

⋮ etc

P. Elliott, K. Burke, M.H. Cohen and A. Wasserman, PRA **82**, 024501 (2010).

Partition Density Functional Theory

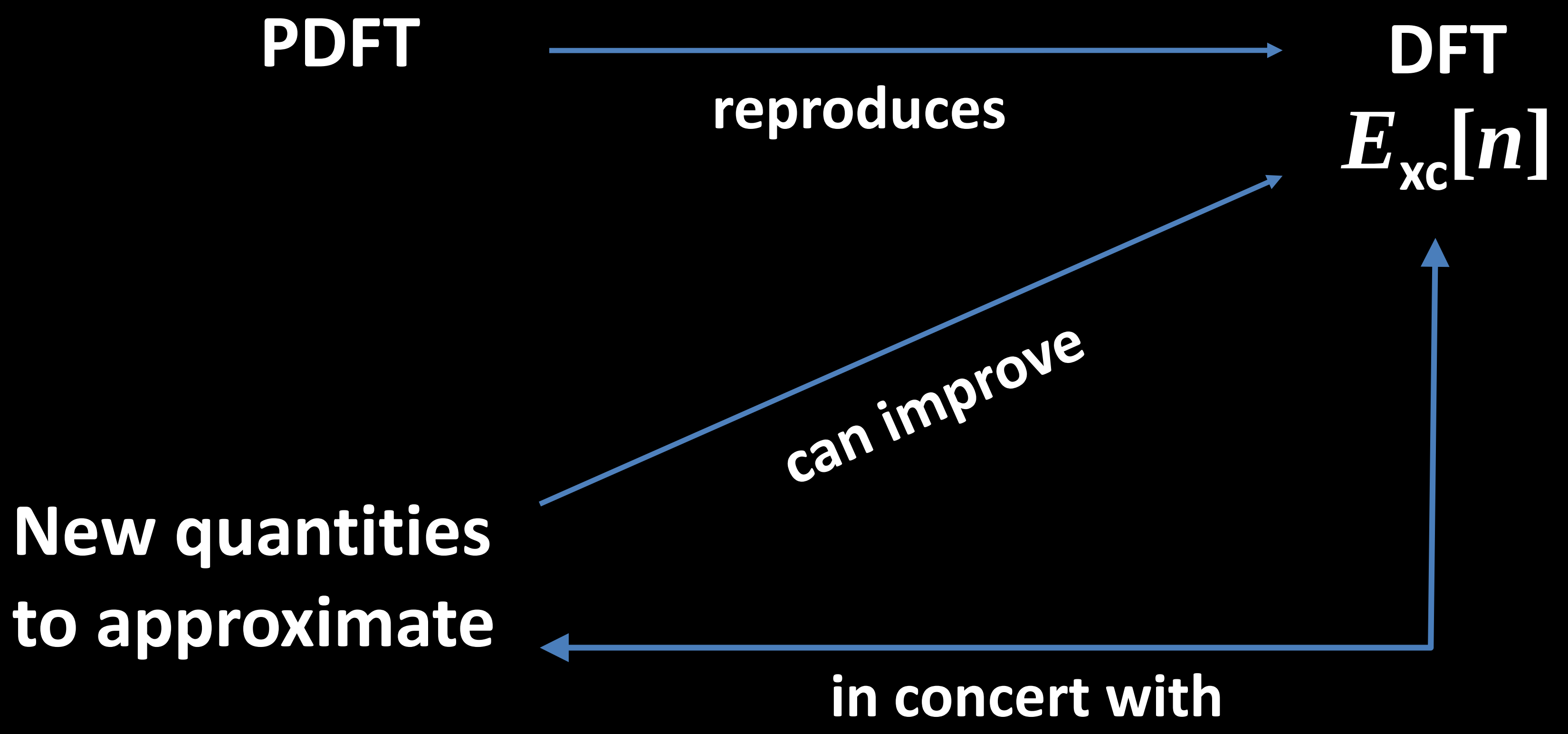
$$v_{s,f,\alpha}(\mathbf{r}) = v^{\alpha}_{\text{nuc}}(\mathbf{r}) + v_p(\mathbf{r}) + v_{\text{HXC}}[n_\alpha](\mathbf{r})$$

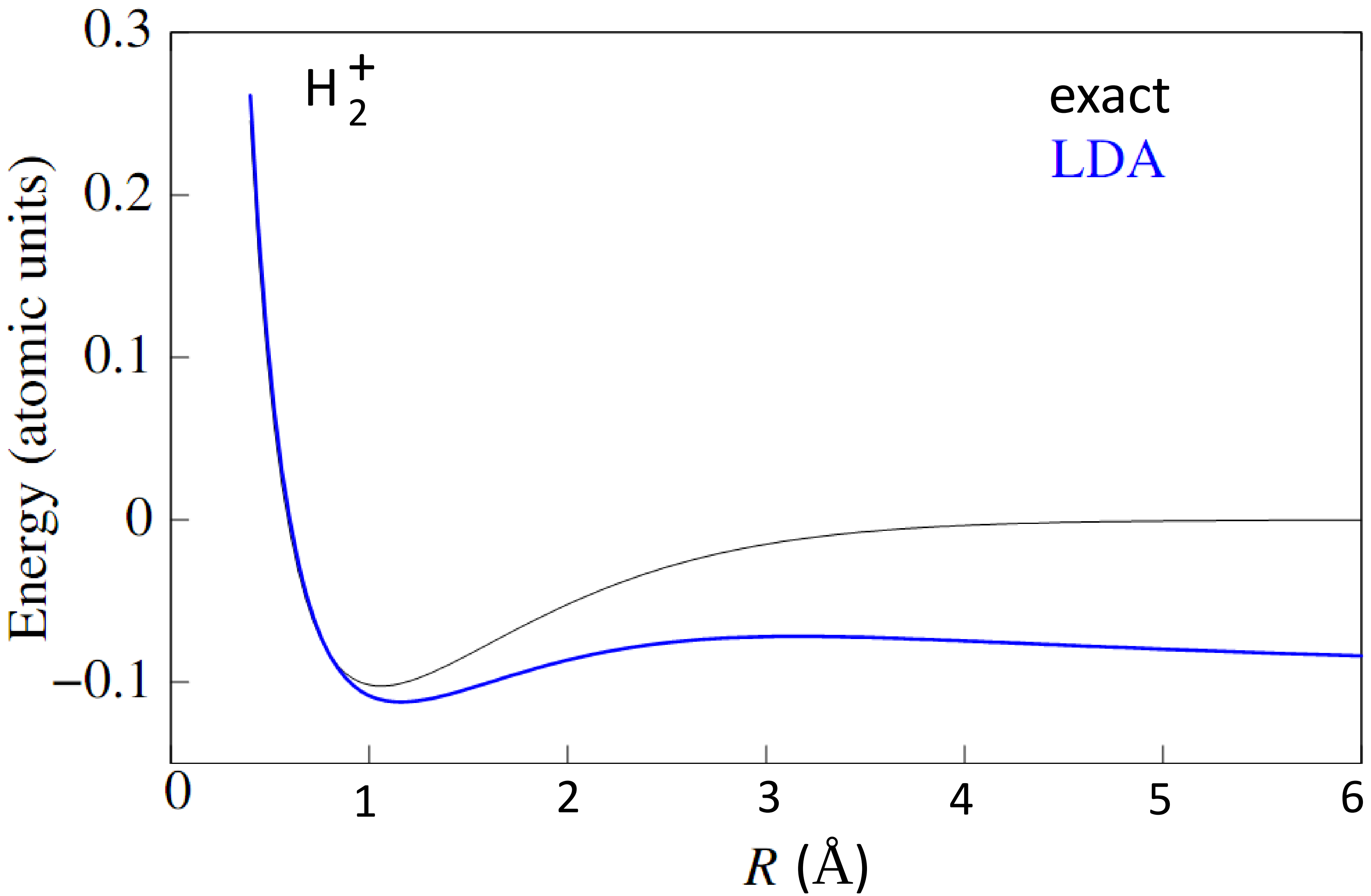
New "external potential" for fragment α

$$\sum_\alpha n_\alpha(\mathbf{r}) = n(\mathbf{r})$$

Get the same molecular density and energy that would have been obtained by solving the KS equations for the molecule. In addition, get the unique set of PDFT fragment densities.

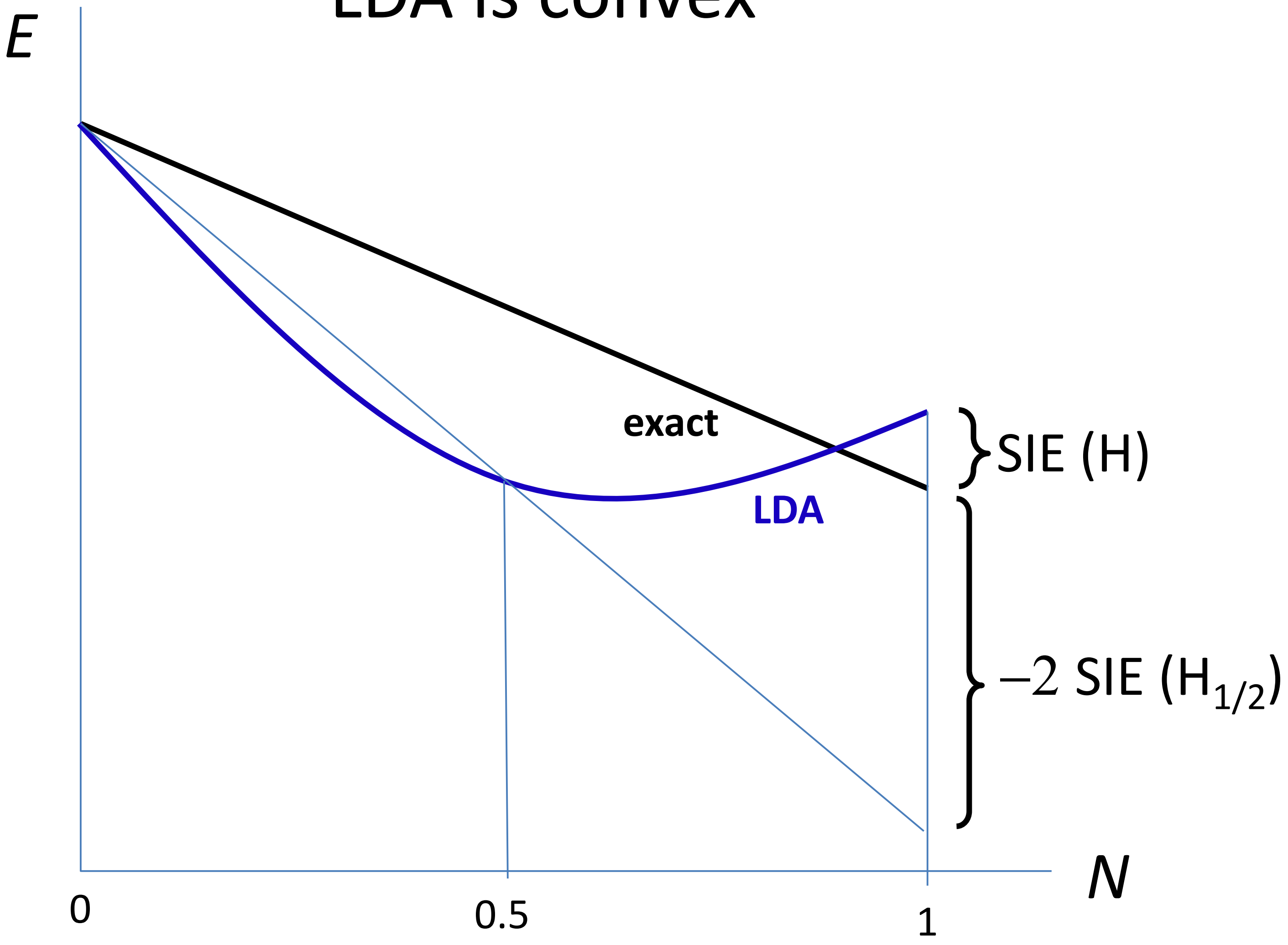
P. Elliott, K. Burke, M.H. Cohen and A. Wasserman, PRA **82**, 024501 (2010).


PDFT
reproduces
DFT
$E_{xc}[n]$
can improve
New quantities
to approximate
in concert with



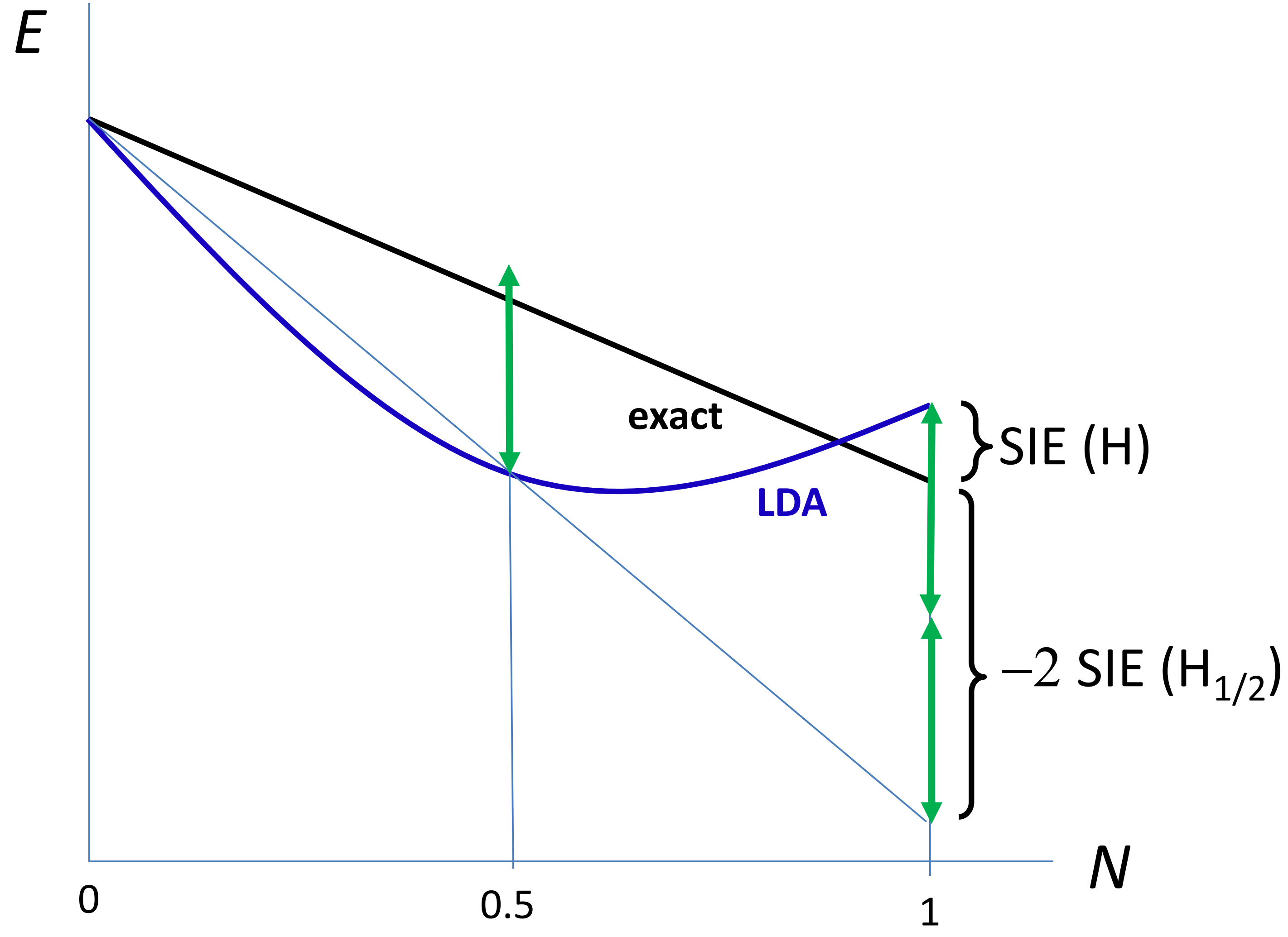
H_2^+
exact
LDA
Energy (atomic units)
0.3
0.2
0.1
0
−0.1
0
1
2
3
4
5
6
R (Å)

LDA is convex



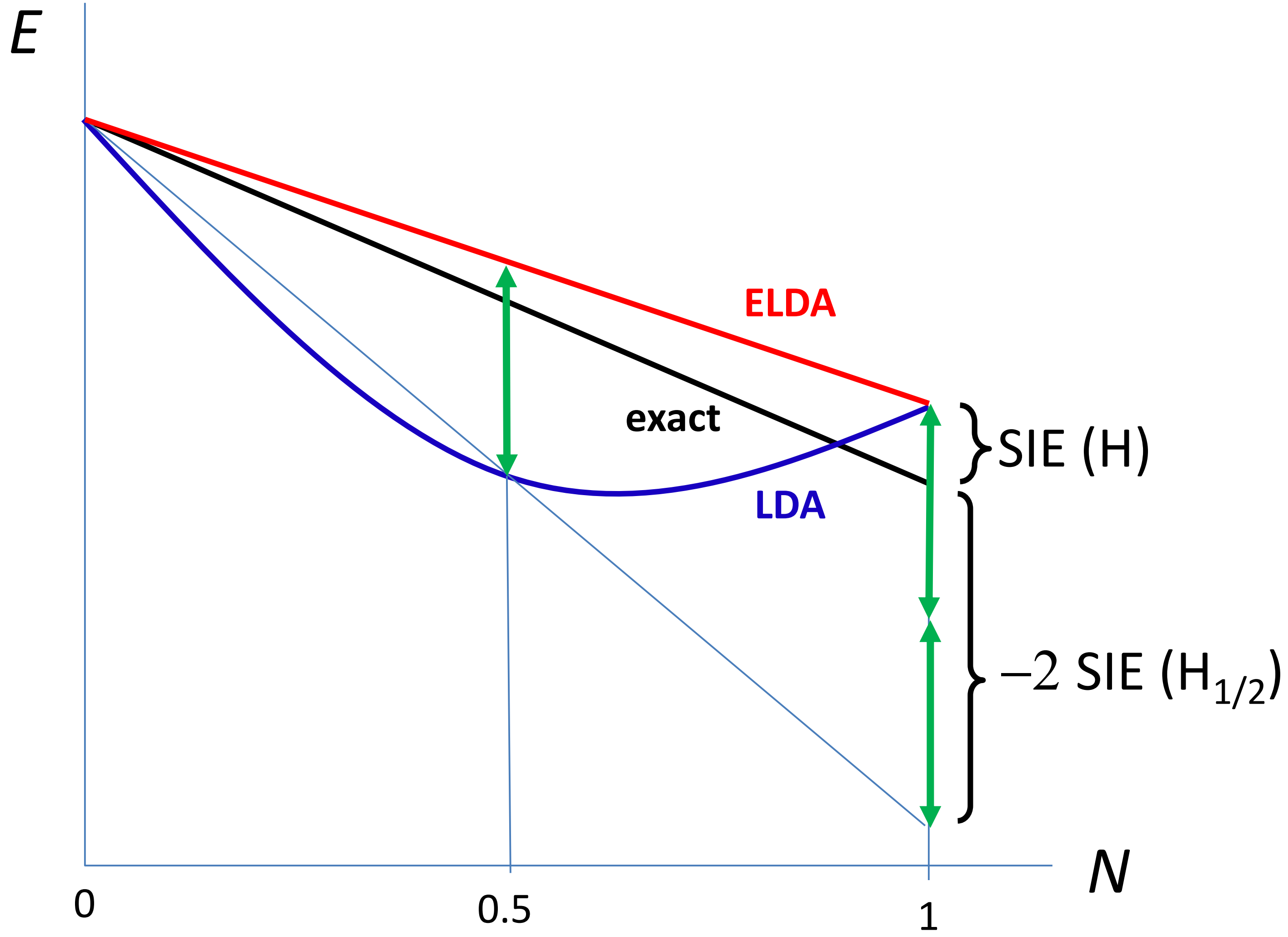
LDA is convex

Delocalization Error



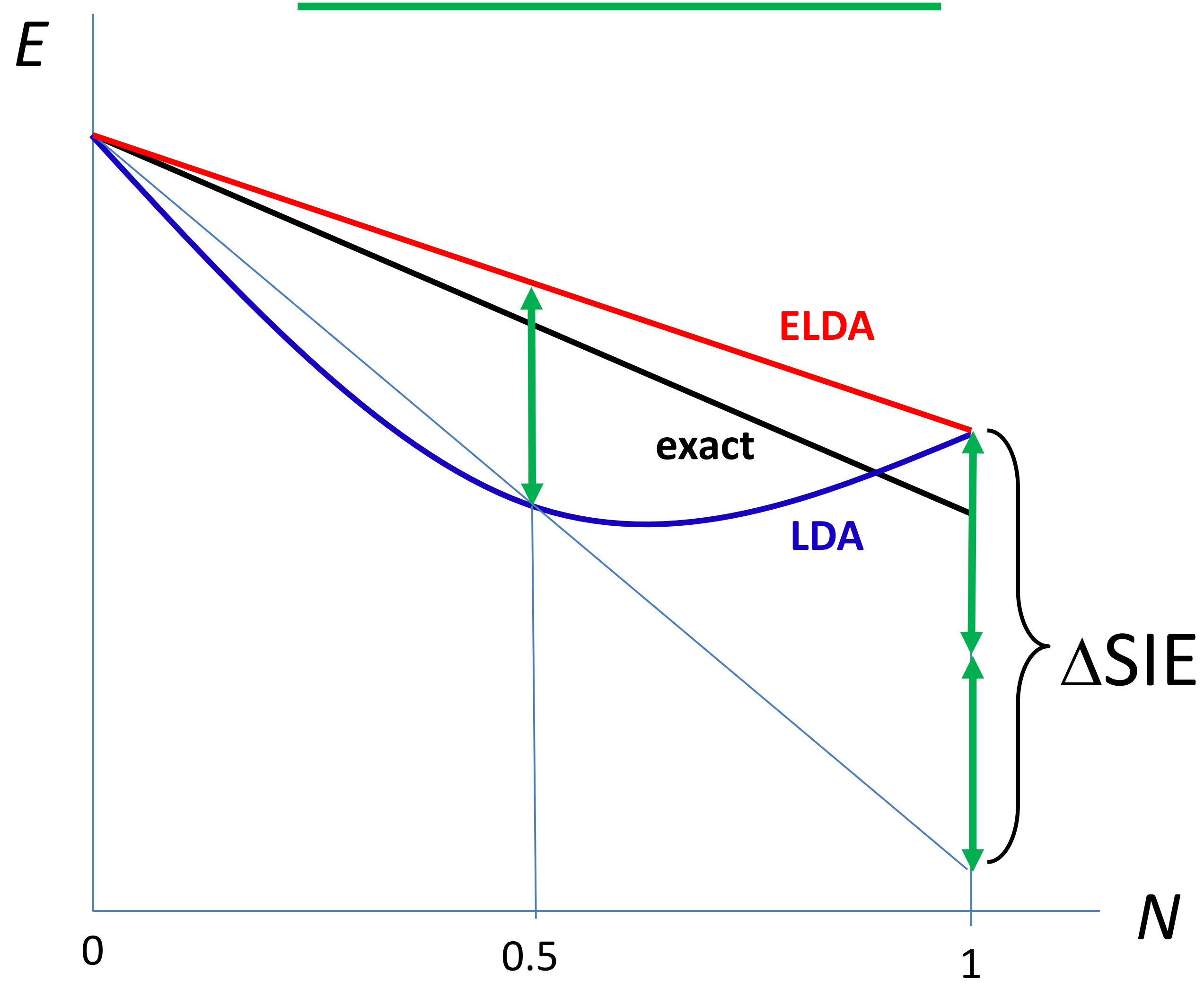
LDA is convex

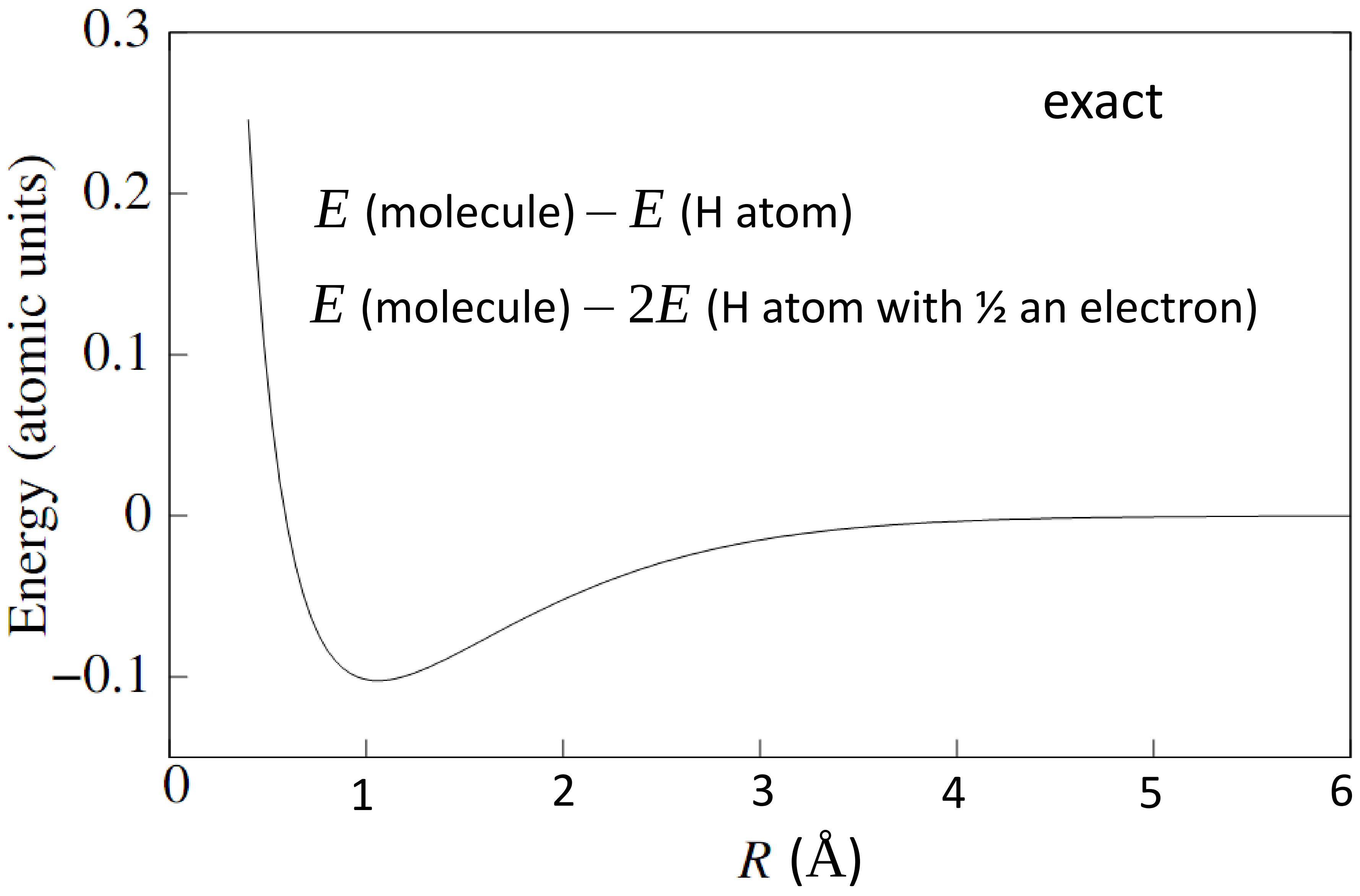
Delocalization Error



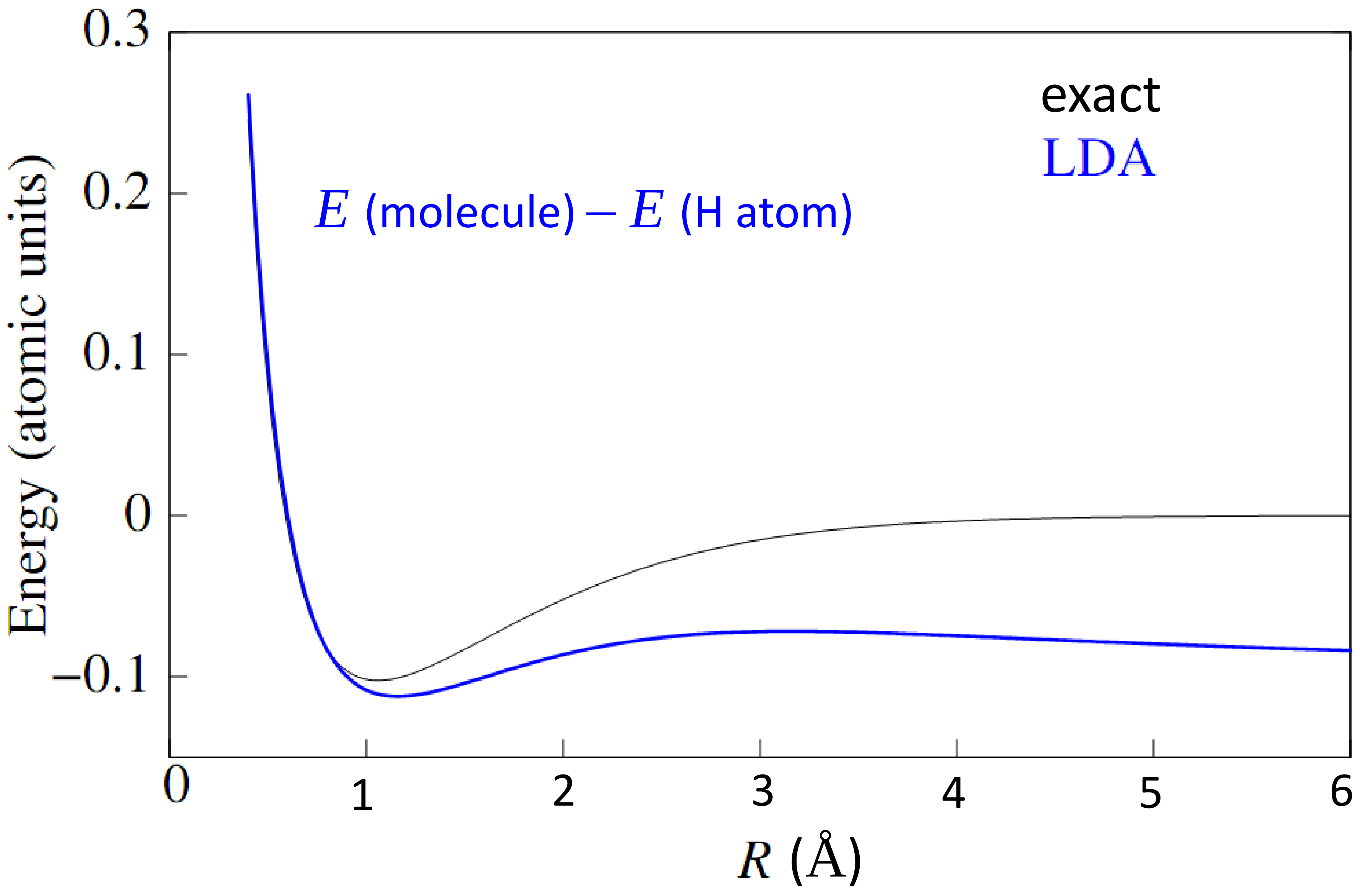
LDA error

Delocalization Error

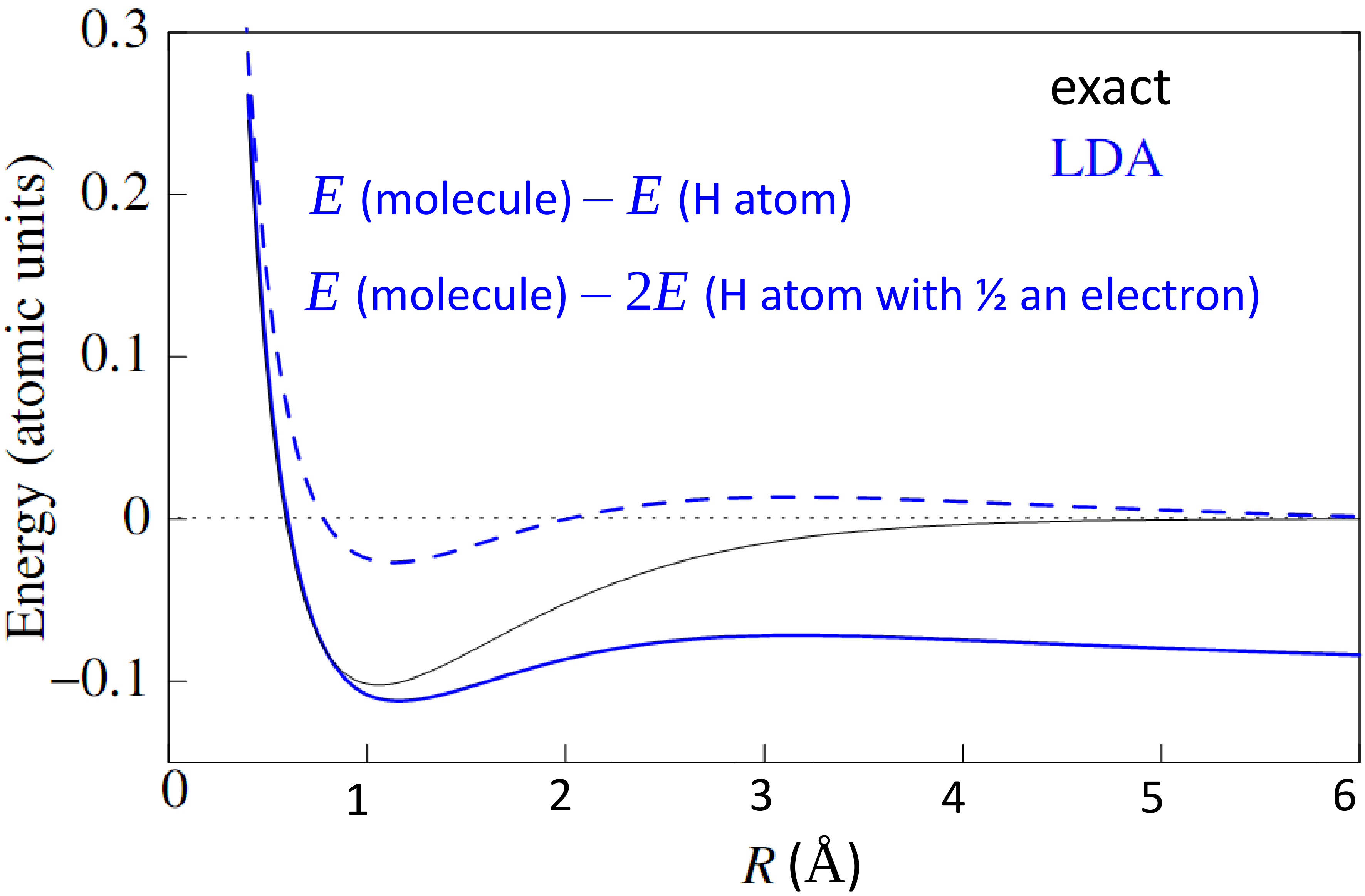




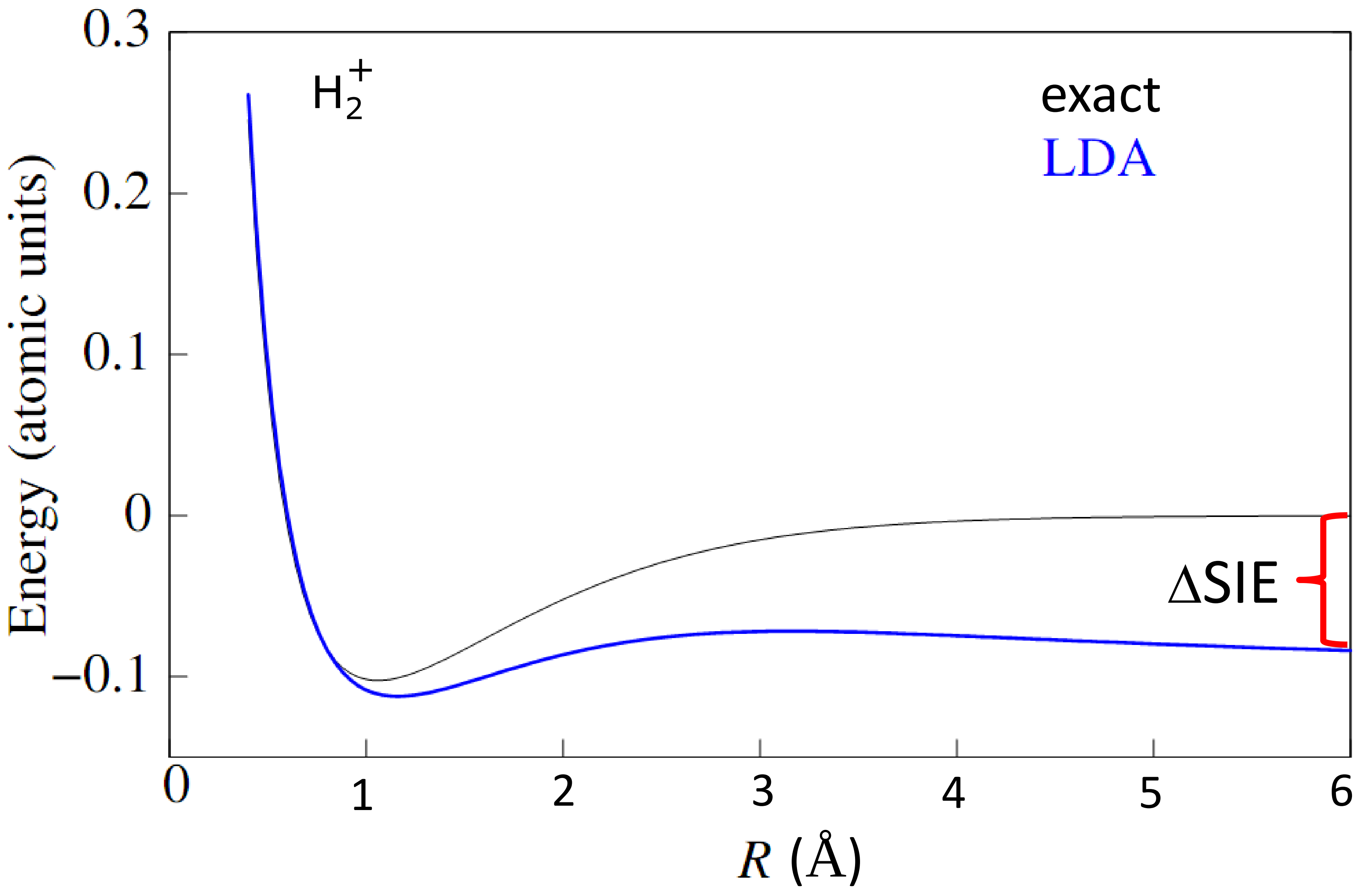
Linear behavior of *E* vs. *N*



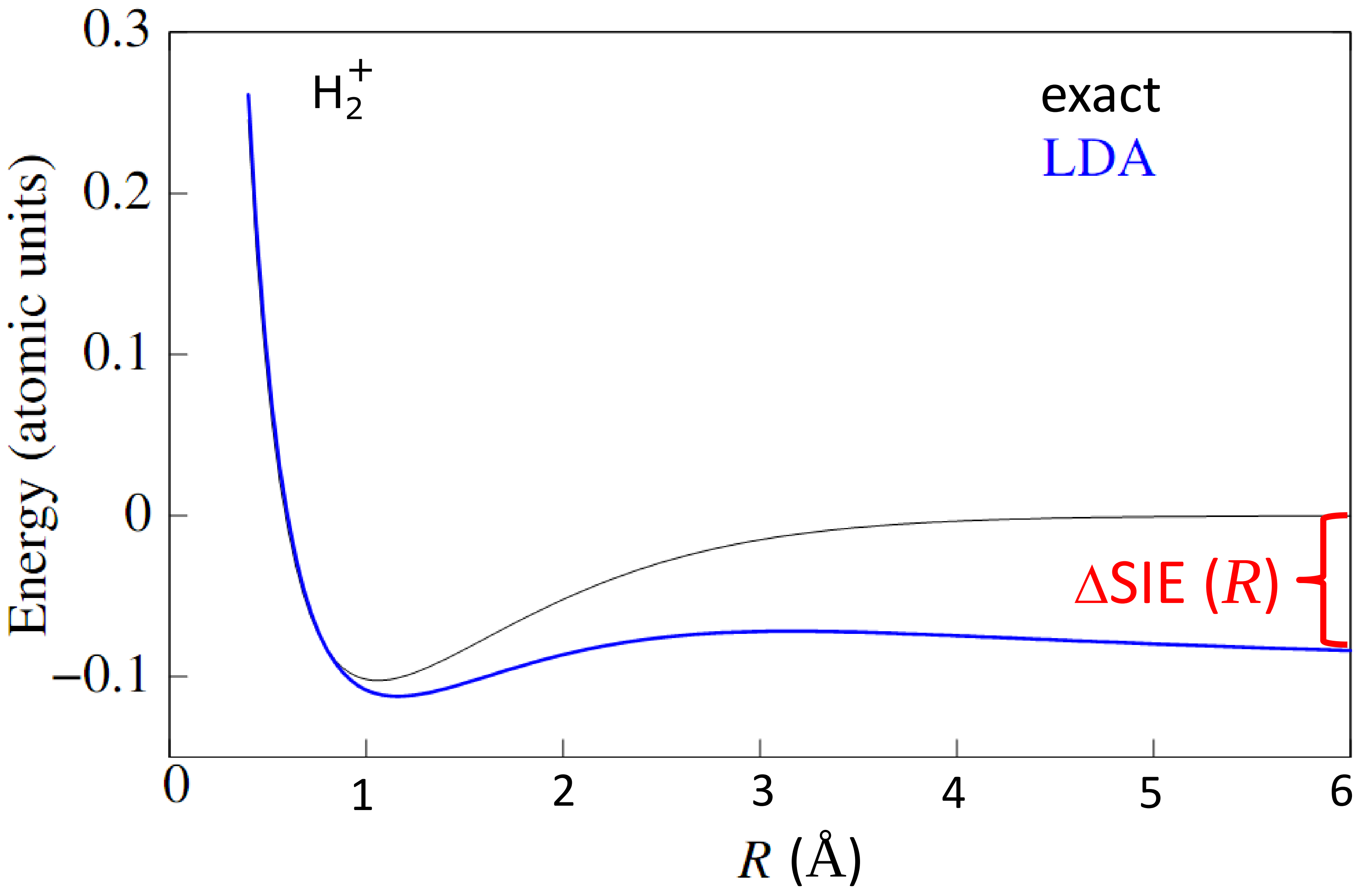
Linear behavior of *E* vs. *N*



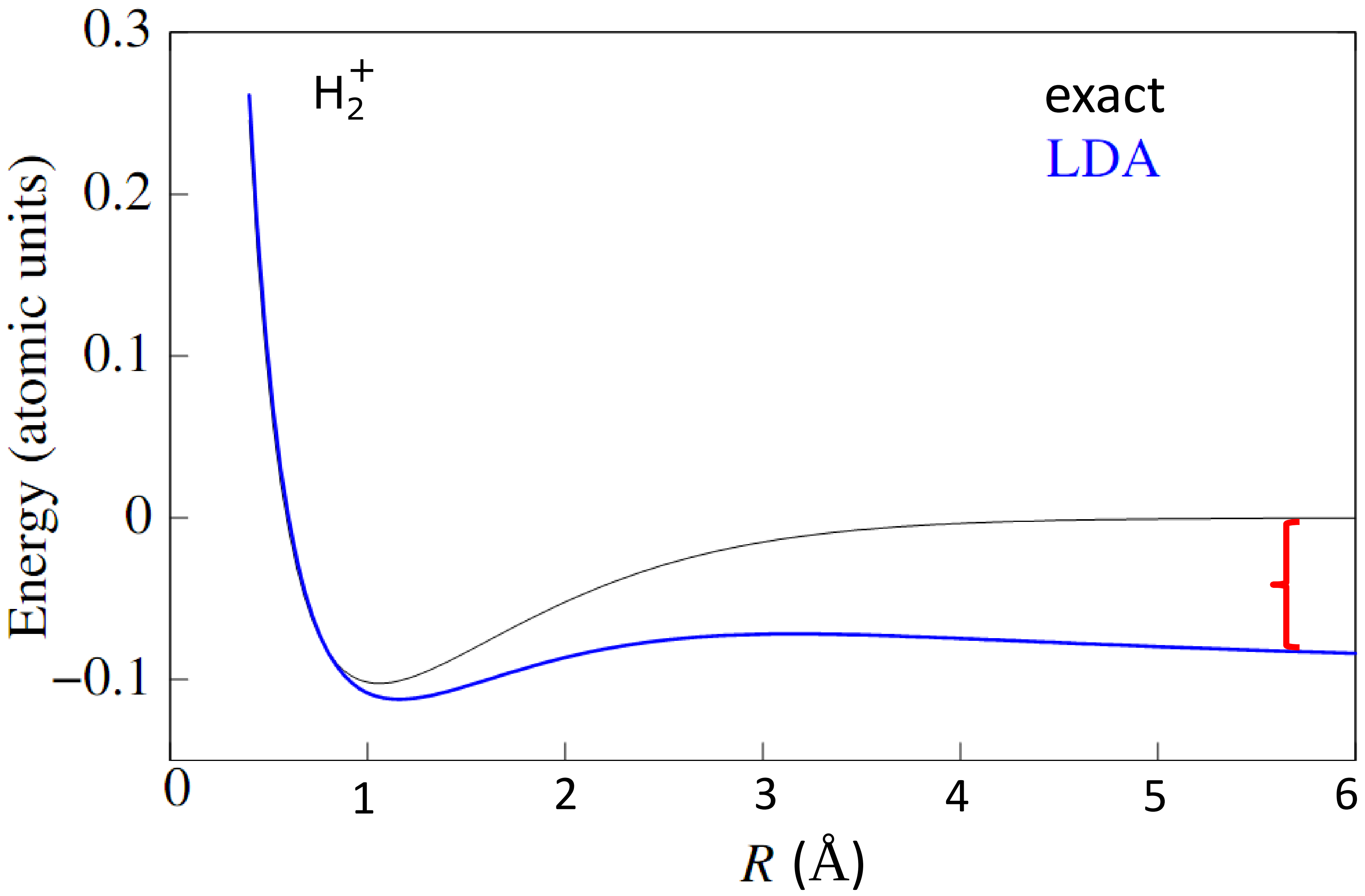
Linear behavior of *E* vs. *N*



Delocalization Error



Delocalization Error



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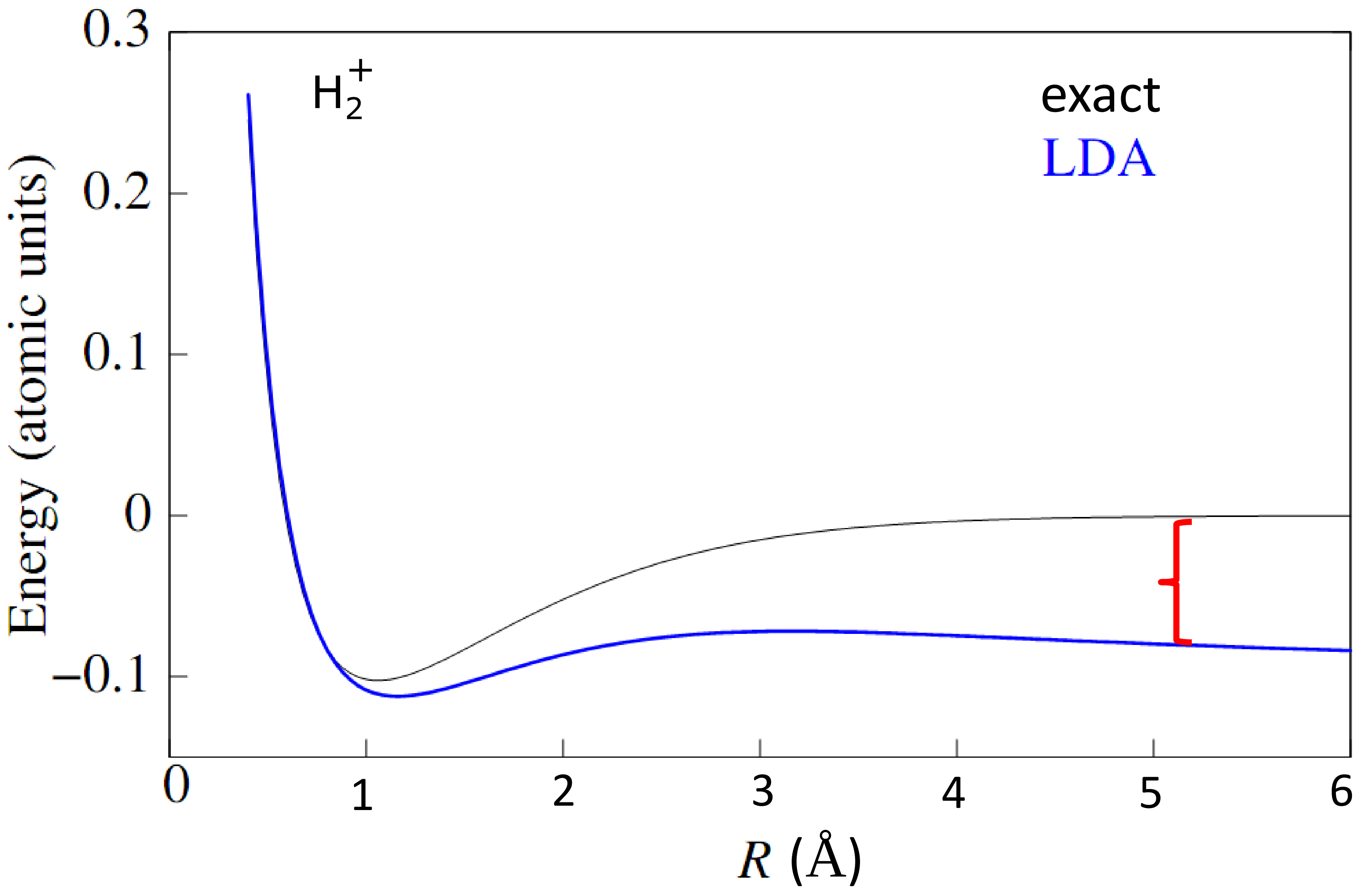

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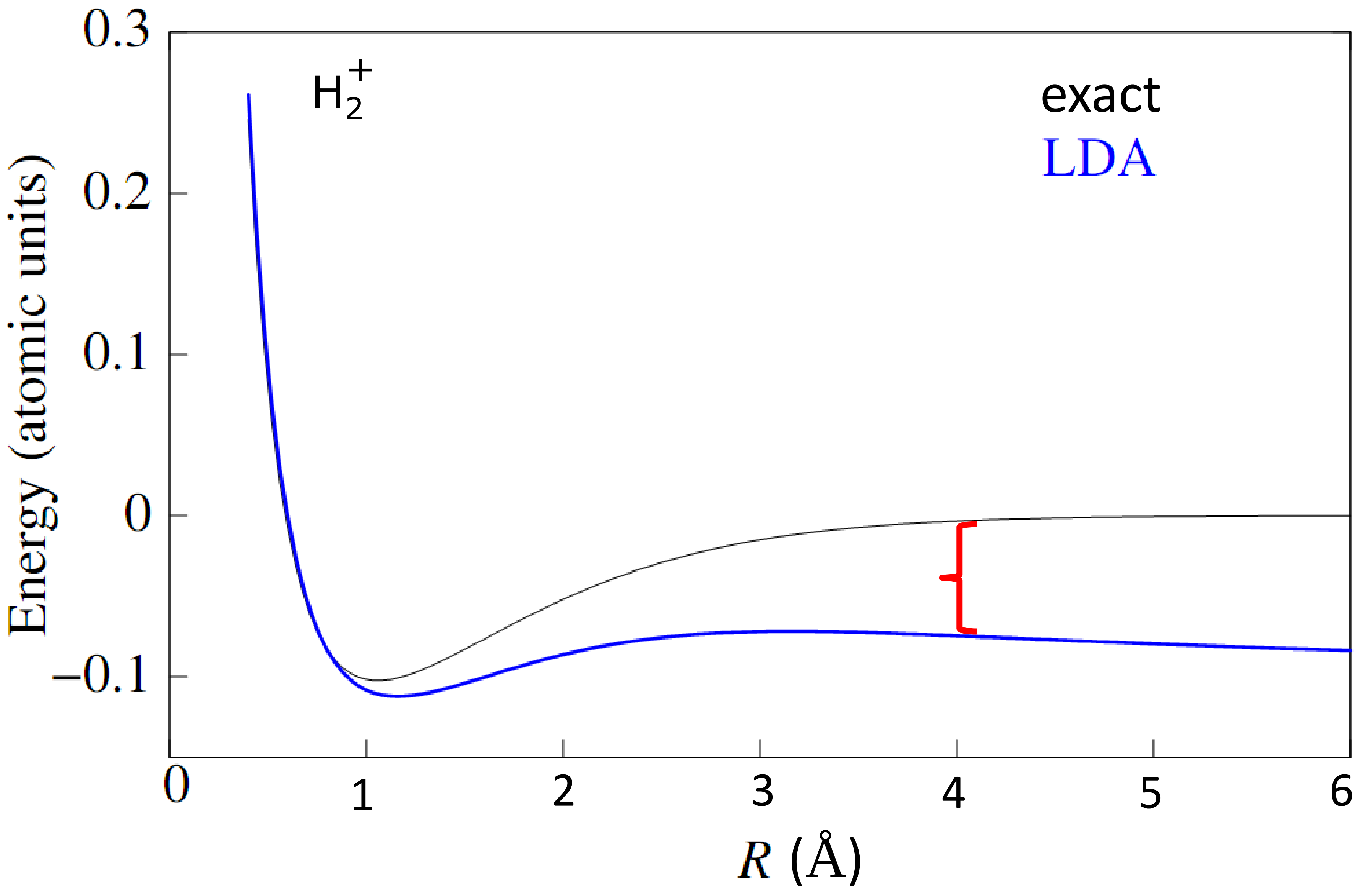

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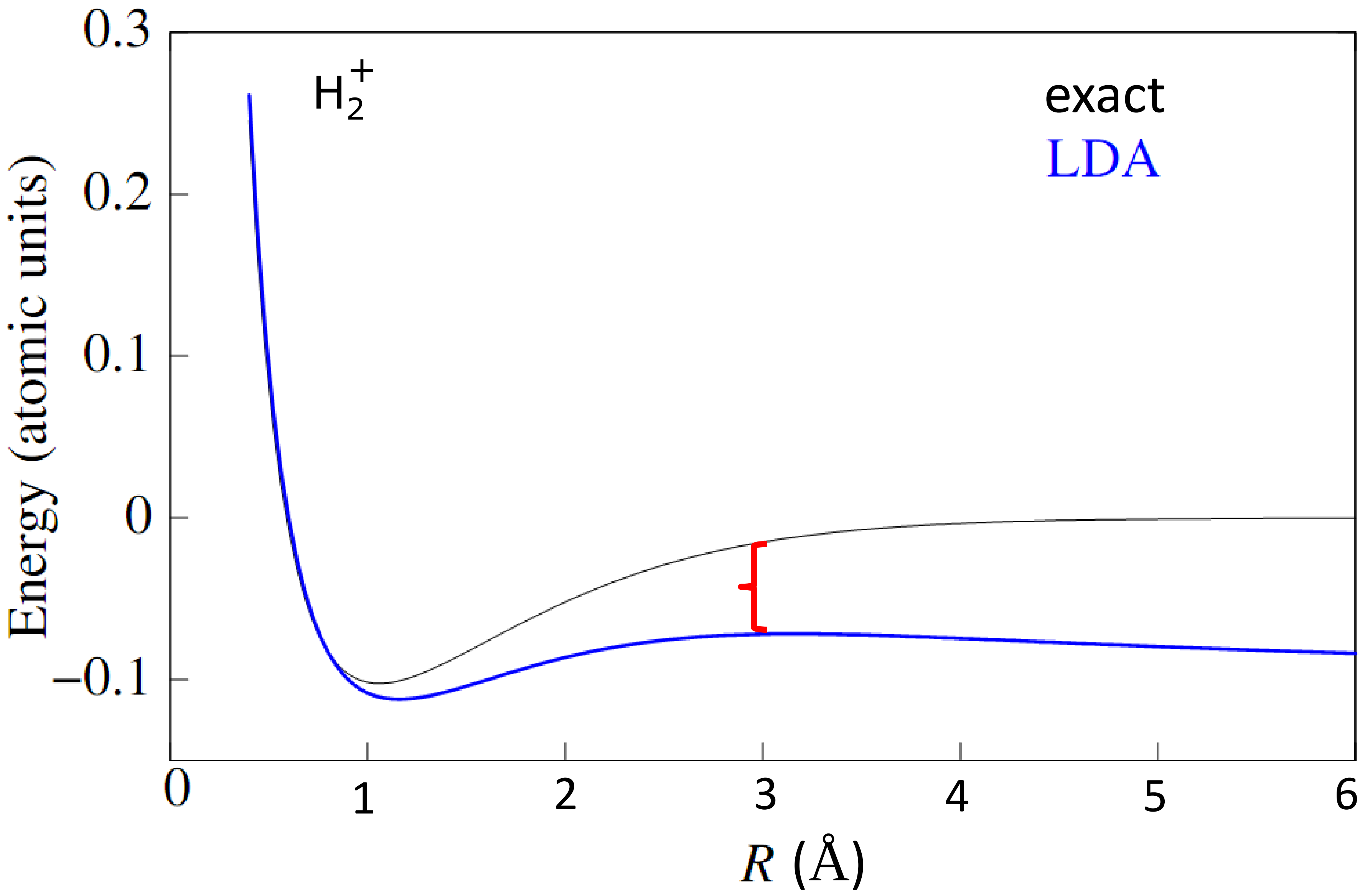

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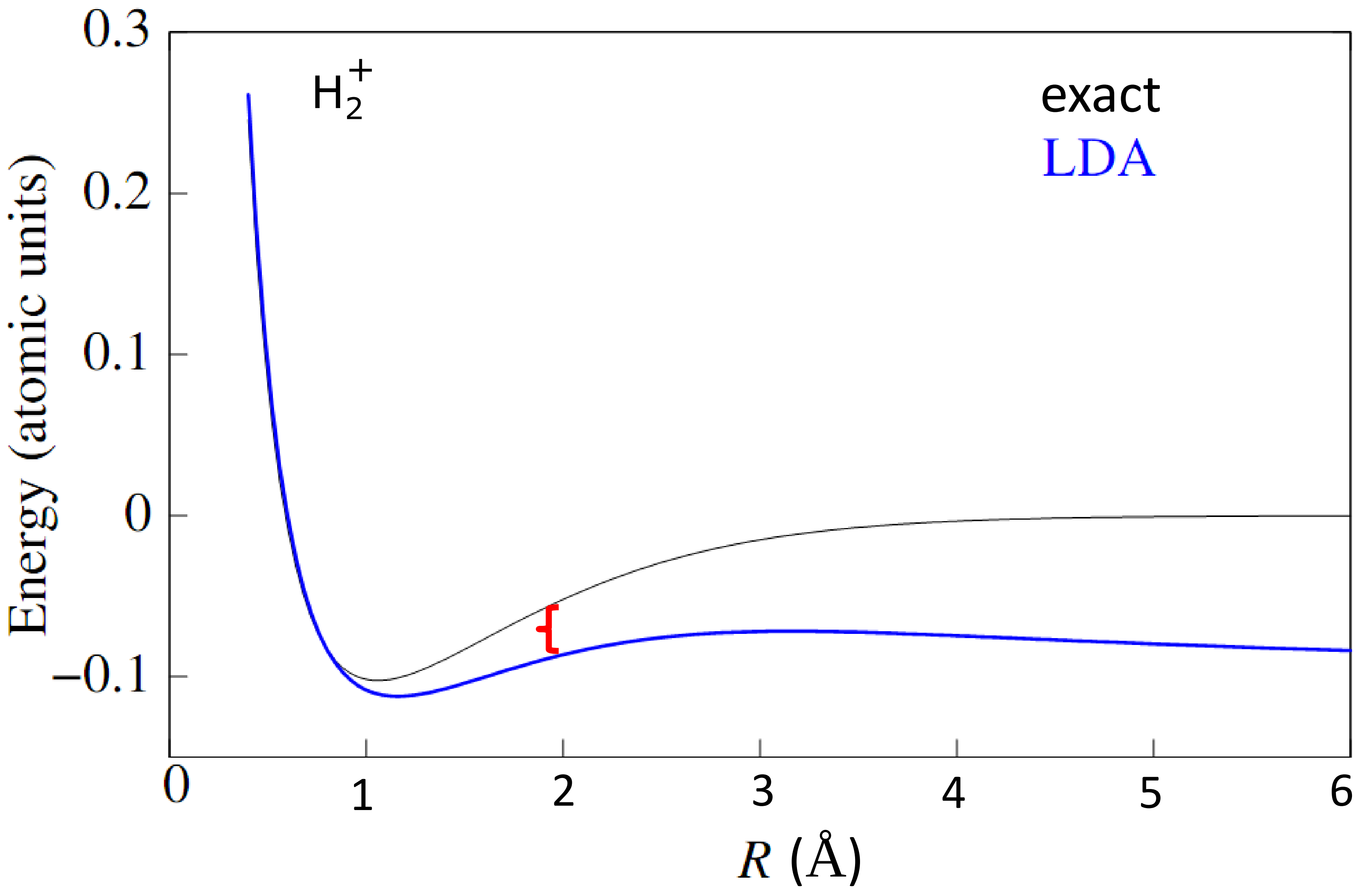

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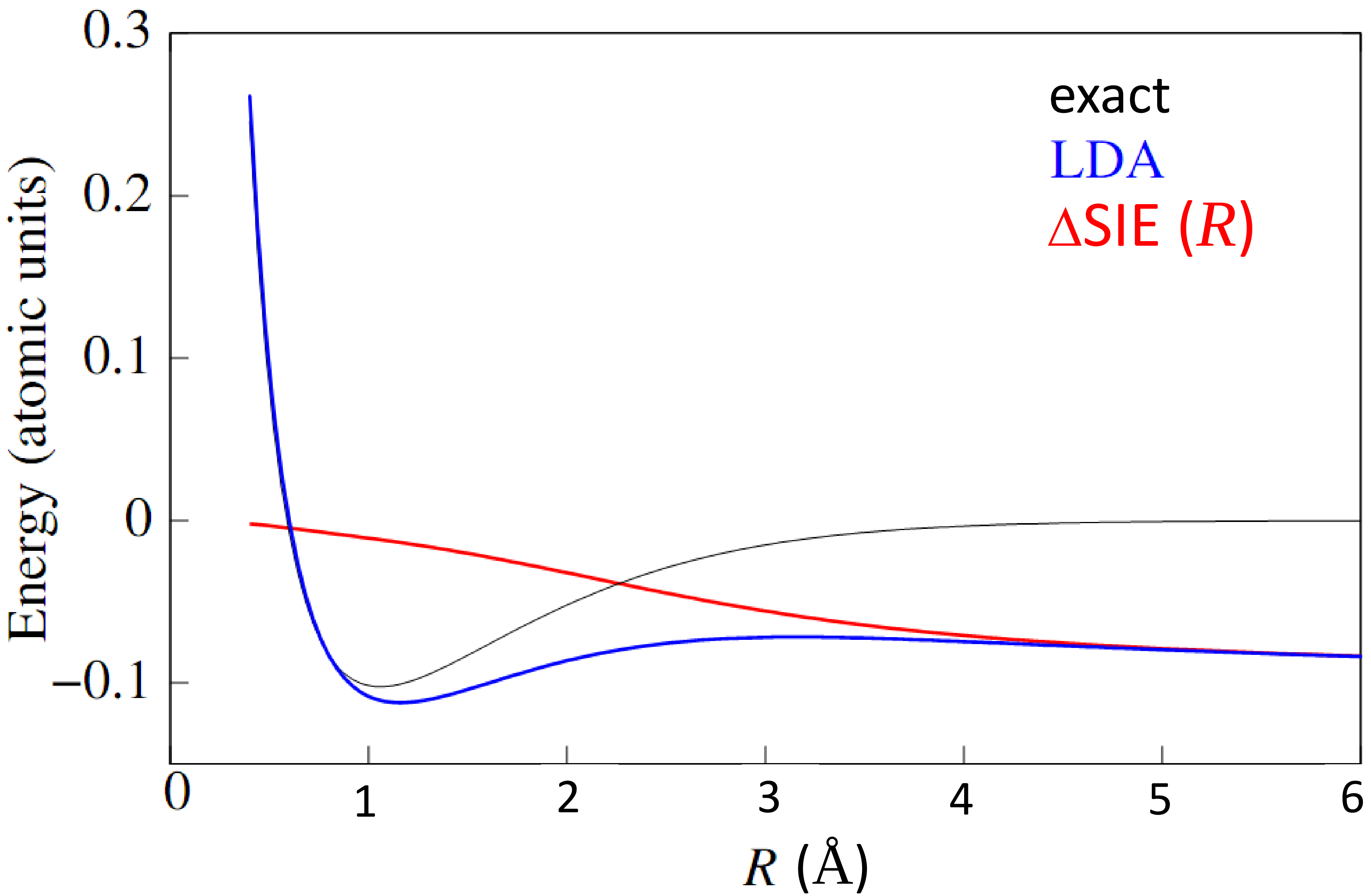

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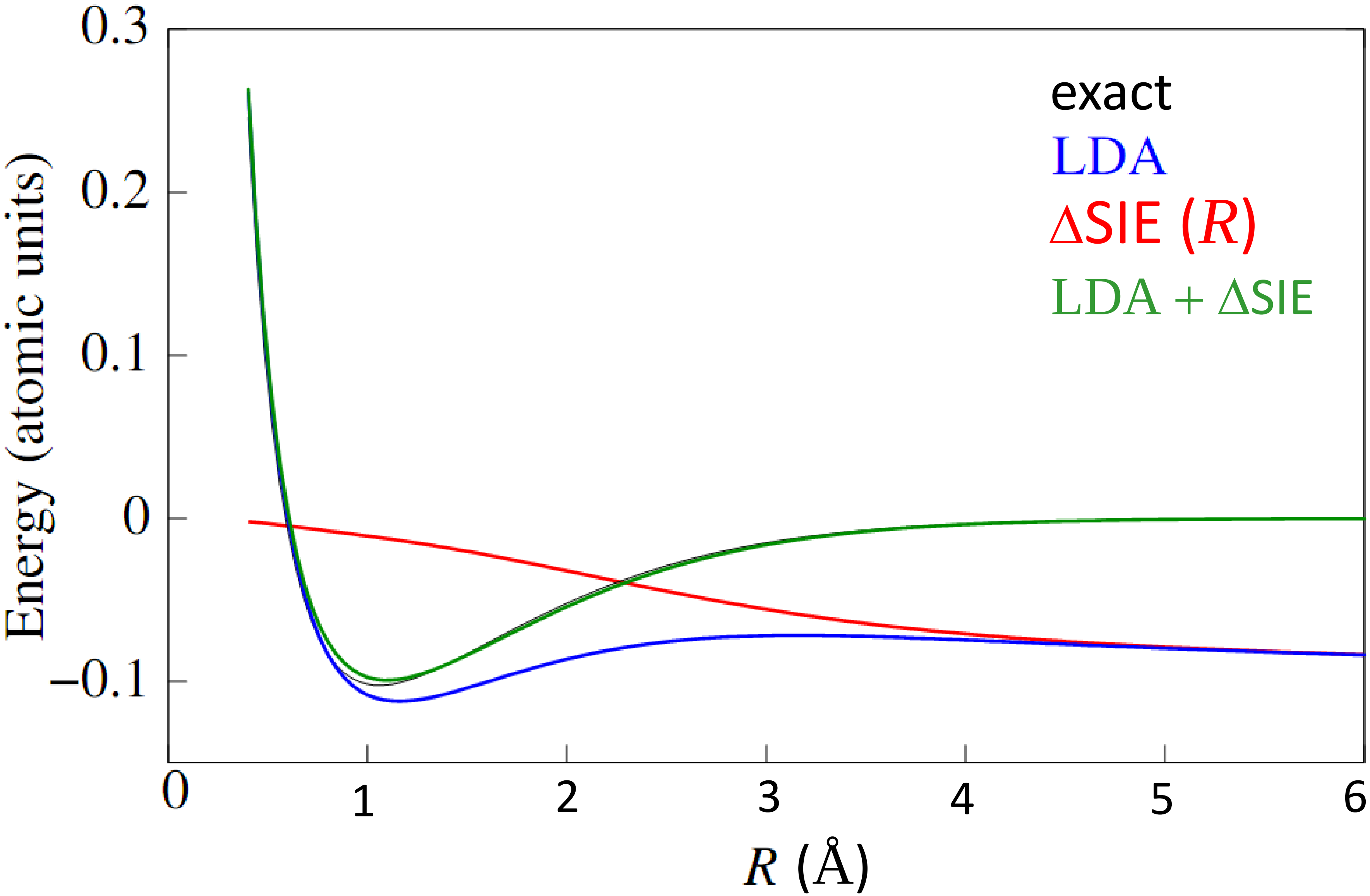


Fixing Delocalization Error

Partition Energy:

$$E_p[\mathbf{n}] = E[n] - E_f[\mathbf{n}]$$

$$E_p[\mathbf{n}] = T_s^{\text{nad}}[\mathbf{n}] + V_{\text{ext}}^{\text{nad}}[\mathbf{n}] + E_{\text{HXC}}^{\text{nad}}[\mathbf{n}]$$

$$T_s^{\text{nad}}[\mathbf{n}] \equiv T_s[n_\uparrow, n_\downarrow] - \sum_{i\alpha} f_{i\alpha} T_s[n_{i\alpha\uparrow}, n_{i\alpha\downarrow}]$$

$$v_p(\mathbf{r}) = \left.\frac{\delta E_p[\mathbf{n}]}{\delta n_\alpha(\mathbf{r})}\right|_{\text{min}}$$

Partition Energy:

$$E_p[\mathbf{n}] = T_s^{\text{nad}}[\mathbf{n}] + V_{\text{ext}}^{\text{nad}}[\mathbf{n}] + E_{\text{HXC}}^{\text{nad}}[\mathbf{n}]$$

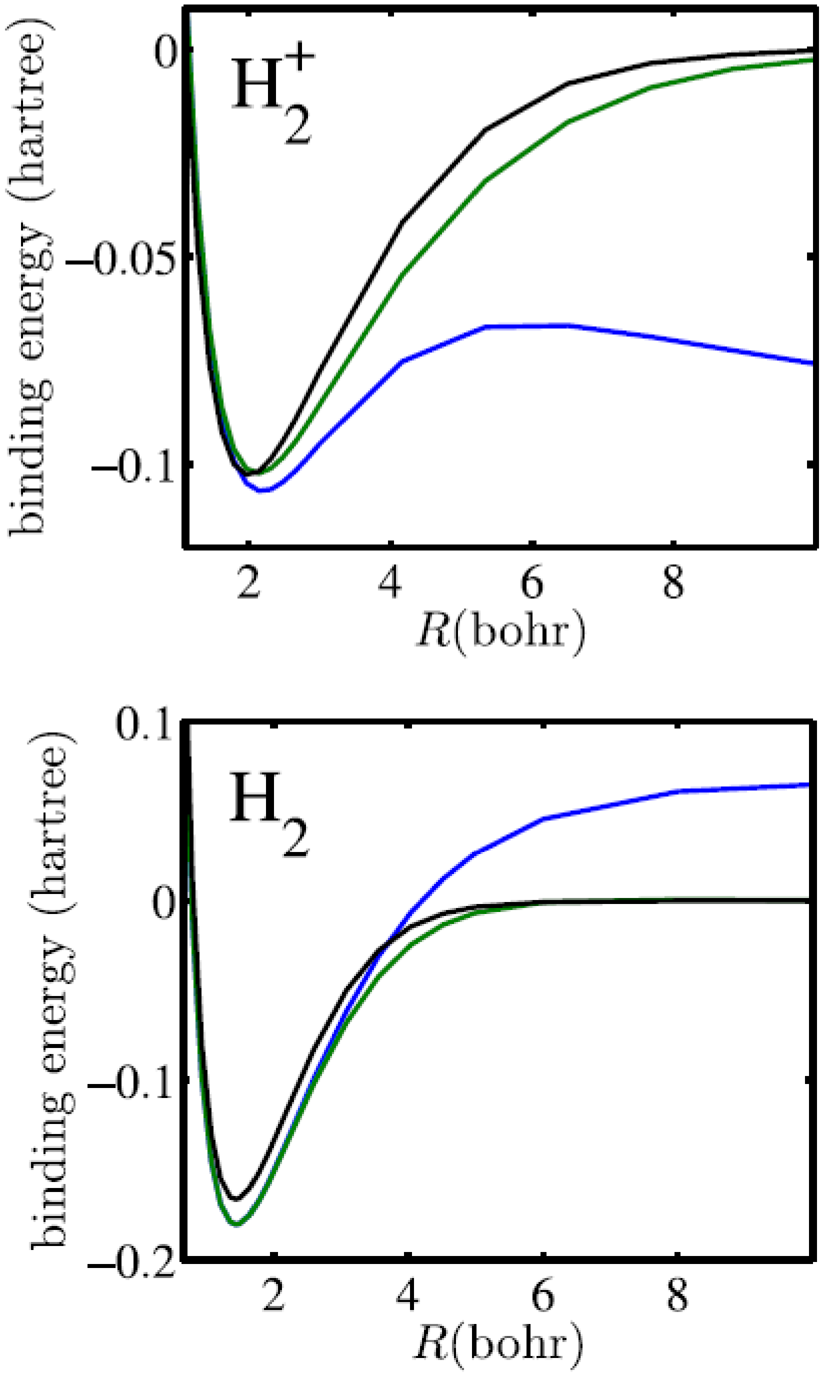
$$T_s^{\text{nad}}[\mathbf{n}] \equiv T_s[n_\uparrow, n_\downarrow] - \sum_{i\alpha} f_{i\alpha} T_s[n_{i\alpha\uparrow}, n_{i\alpha\downarrow}]$$

Overlap approximation:

$$E_{\text{HXC}}^{\text{nad,OA}}[\mathbf{n}] = E_{\text{H}}^{\text{nad}}[\mathbf{n}] + S[\mathbf{n}] E_{\text{XC}}^{\text{nad}}[\mathbf{n}] + (1 - S[\mathbf{n}]) \Delta E_{\text{H}}^{\text{nad}}[\mathbf{n}]$$

$$S[\mathbf{n}] = \text{erf}\left(2 \int [n_A(\mathbf{r}) n_B(\mathbf{r})]^{1/2} \, d\mathbf{r}\right)$$

J. Nafziger and A. Wasserman, JCP **143**, 234105 (2015).

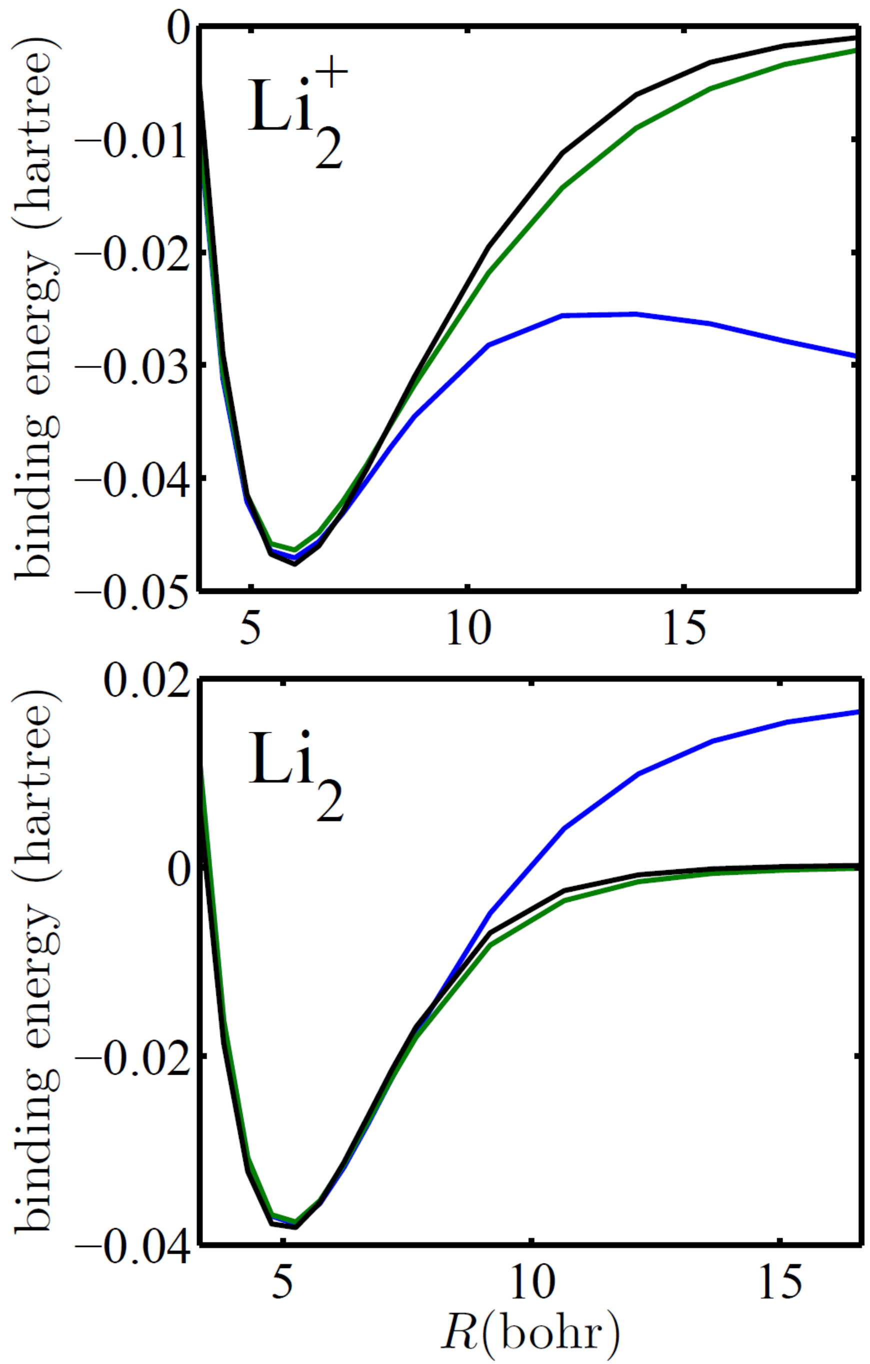


exact

LDA

Approximate PDFT

J. Nafziger and A. Wasserman, JCP **143**, 234105 (2015).



exact

LDA

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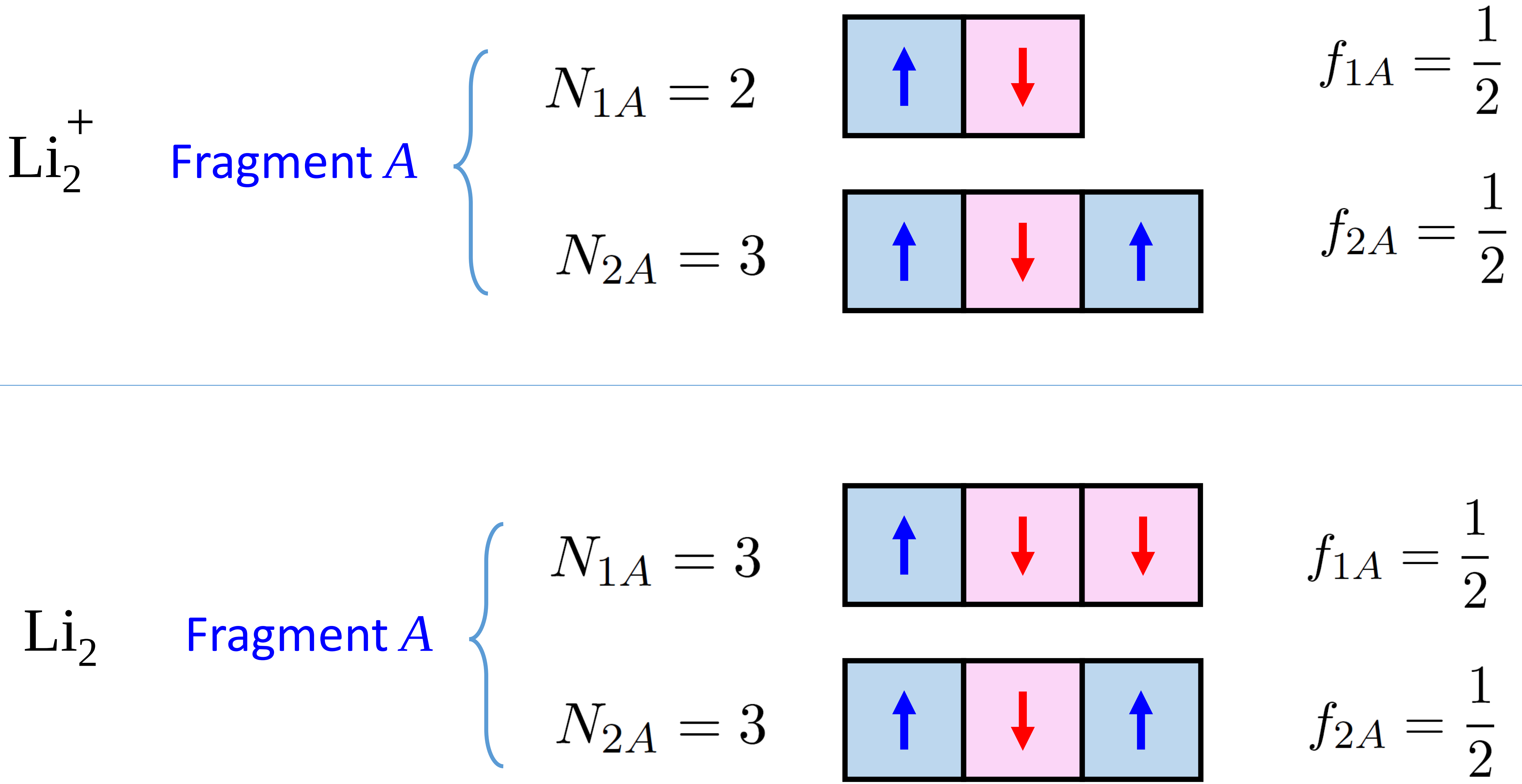
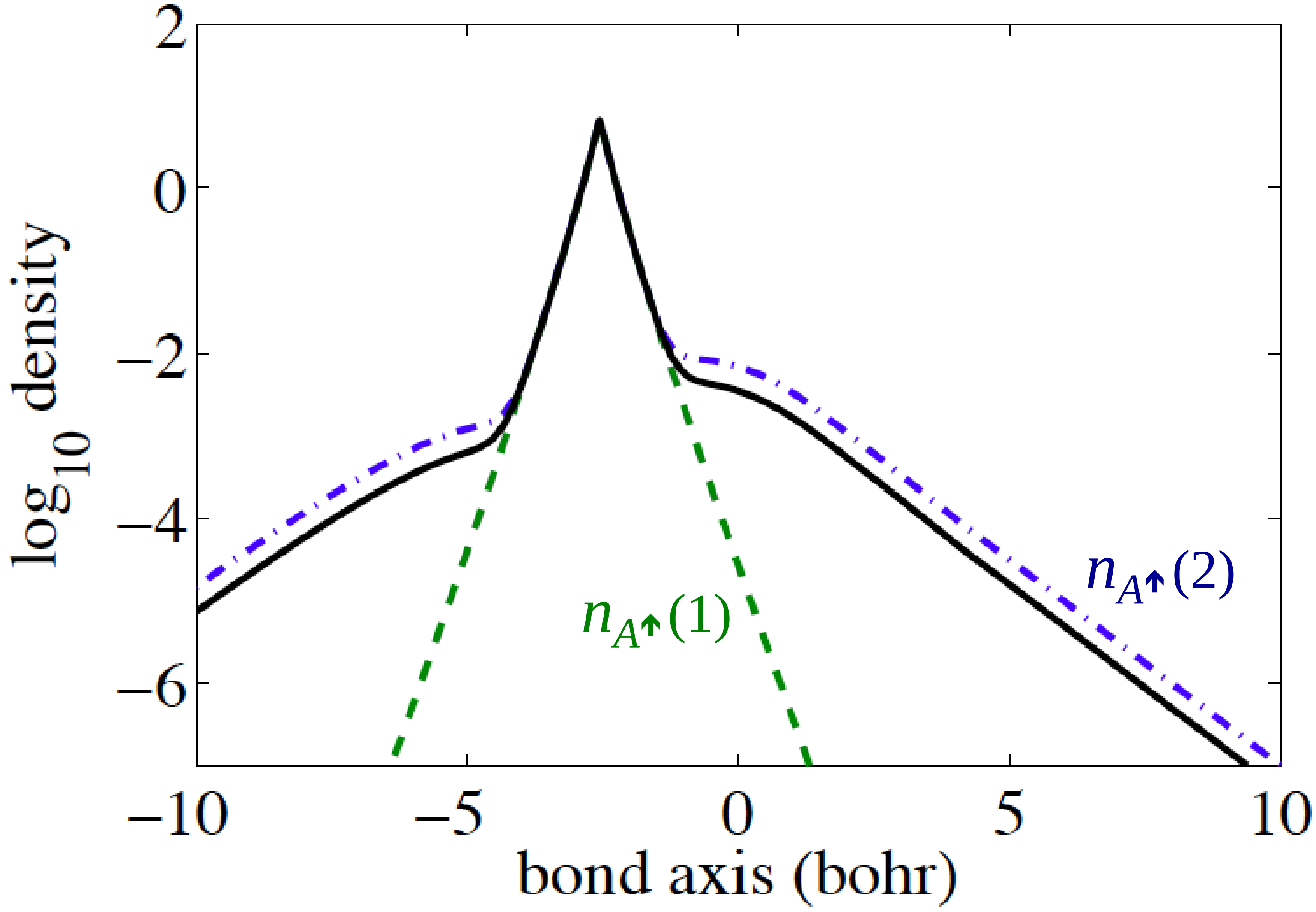
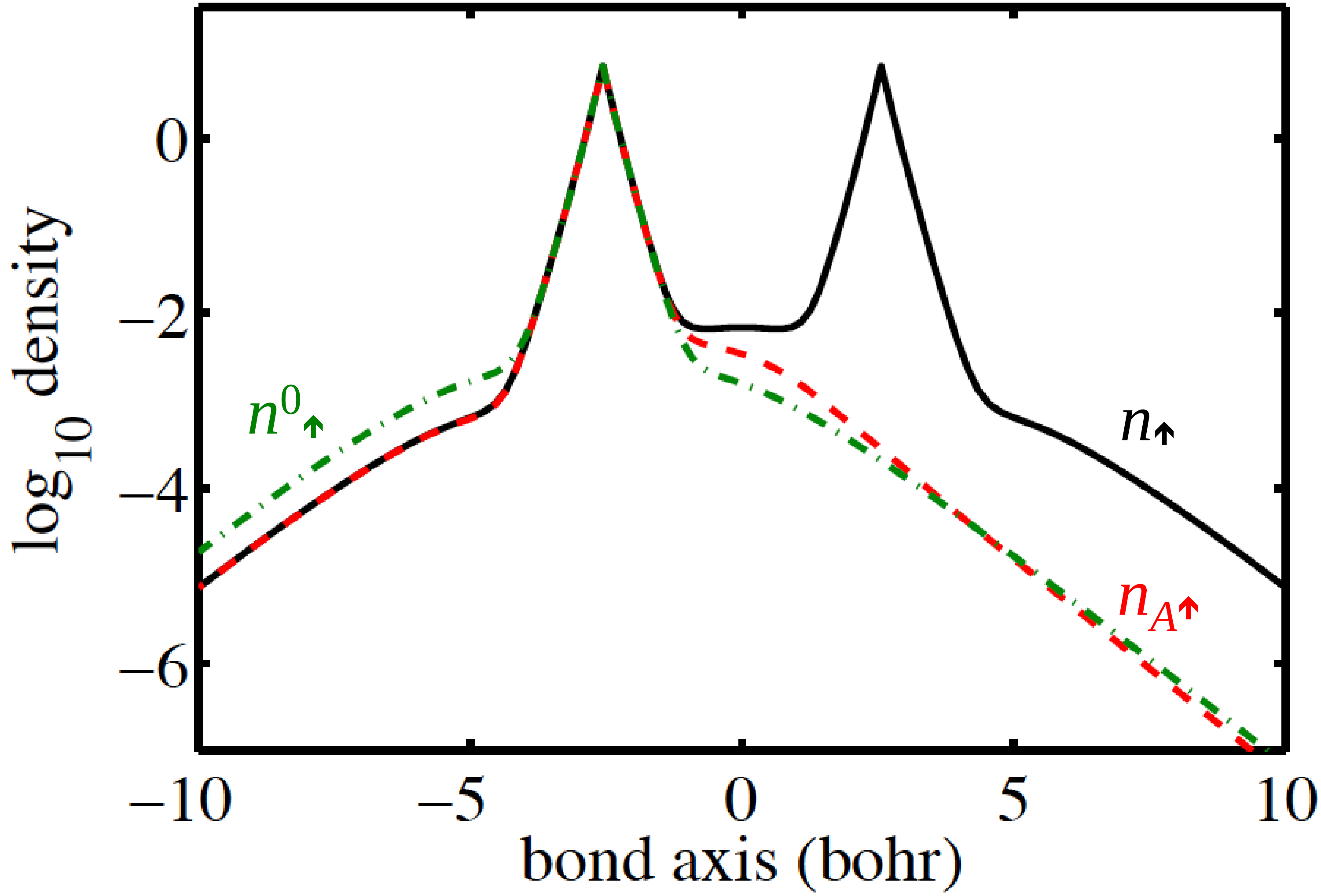


Li_2^+
Fragment A
$N_{1A} = 2$
$f_{1A} = \frac{1}{2}$
$N_{2A} = 3$
$f_{2A} = \frac{1}{2}$
Li_2
Fragment A
$N_{1A} = 3$
$f_{1A} = \frac{1}{2}$
$N_{2A} = 3$
$f_{2A} = \frac{1}{2}$

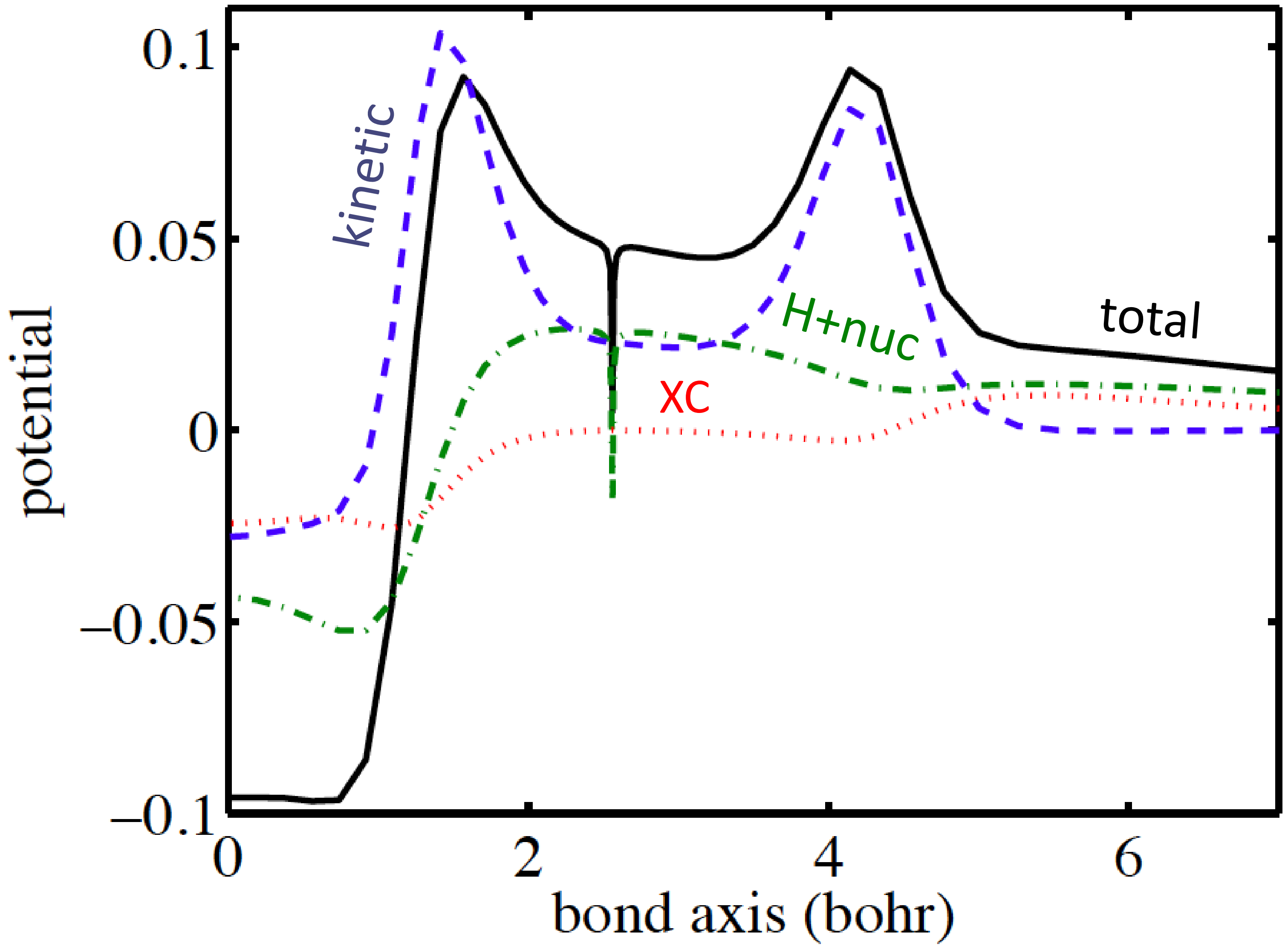
Fragment densities – Li_2



Fragment densities – Li_2



Partition potential components – Li_2

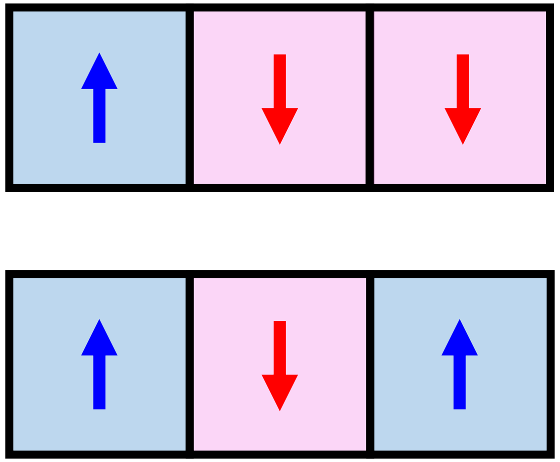


Non-additive Hartree correction:

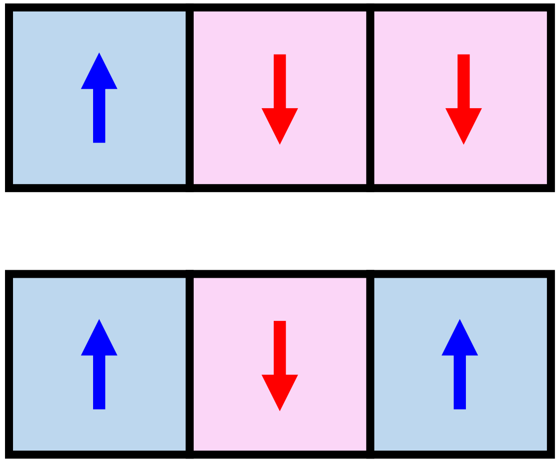
$$\Delta E_{\mathrm{H}}^{\mathrm{nad}}[\mathbf{n}] \equiv \frac{1}{4}\sum_{\alpha\neq\beta}\sum_{i,j} g_{ij} f_{i\alpha}\int \frac{n_{iA}(\mathbf{r})n_{jB}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' - E_{\mathrm{H}}^{\mathrm{nad}}[\mathbf{n}]$$

$$g_{ij} = \begin{cases} 0 & N_{i\alpha} + N_{j\beta} \neq N \\ 1 & N_{i\alpha} + N_{j\beta} = N \end{cases}$$

Li_2



$$\Delta E_{\mathrm{H}}^{\mathrm{nad}} = 0$$

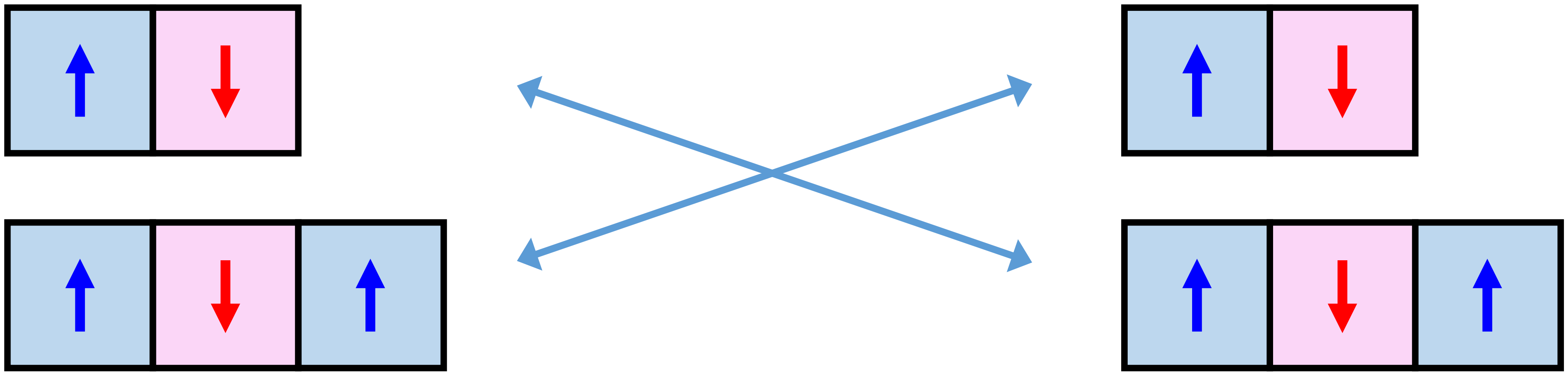


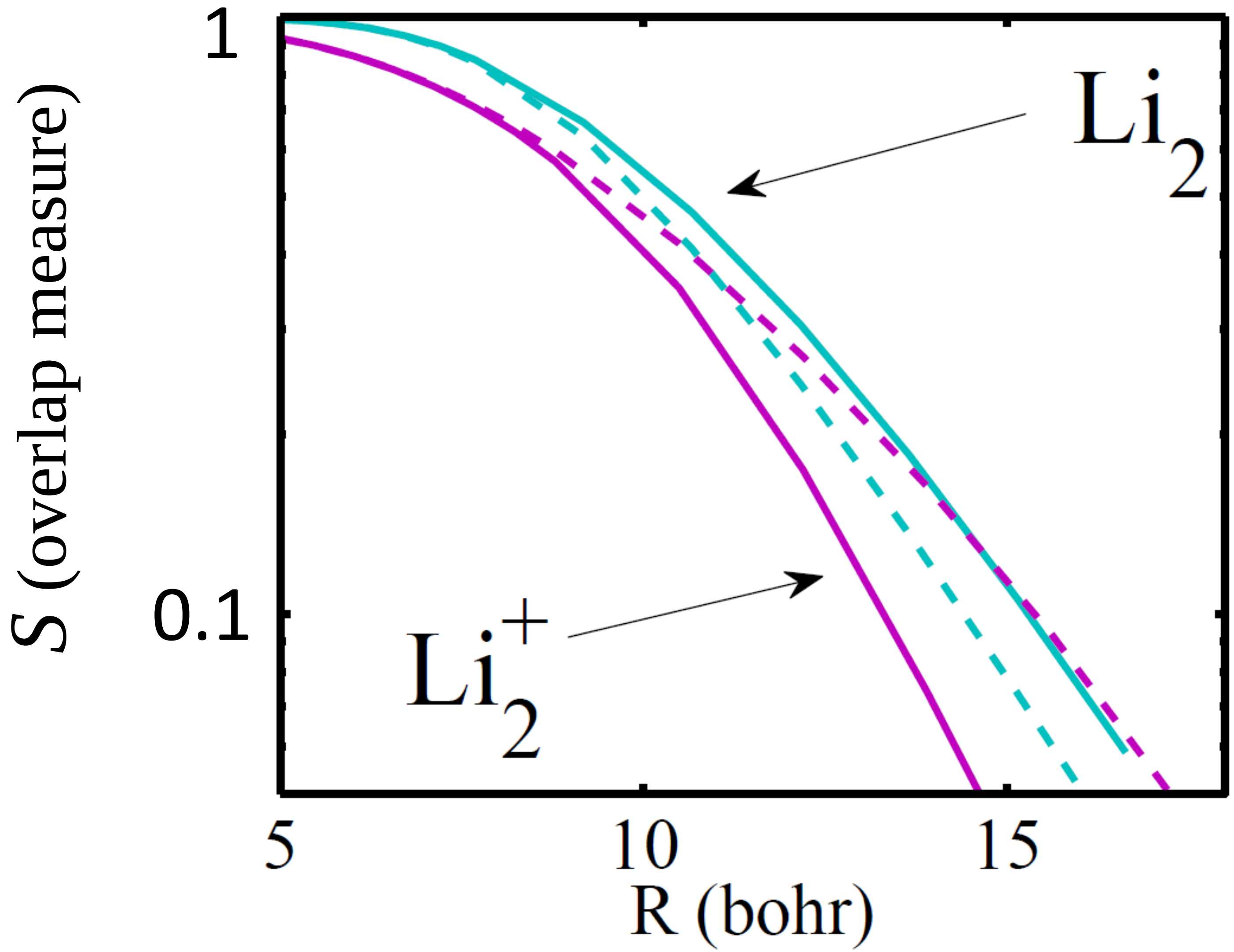
Non-additive Hartree correction:

$$\Delta E_{\mathrm{H}}^{\mathrm{nad}}[\mathbf{n}] \equiv \frac{1}{4}\sum_{\alpha\neq\beta}\sum_{i,j} g_{ij} f_{i\alpha} \int \frac{n_{iA}(\mathbf{r})n_{jB}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' - E_{\mathrm{H}}^{\mathrm{nad}}[\mathbf{n}]$$

$$g_{ij} = \begin{cases} 0 & N_{i\alpha} + N_{j\beta} \neq N \\ 1 & N_{i\alpha} + N_{j\beta} = N \end{cases}$$

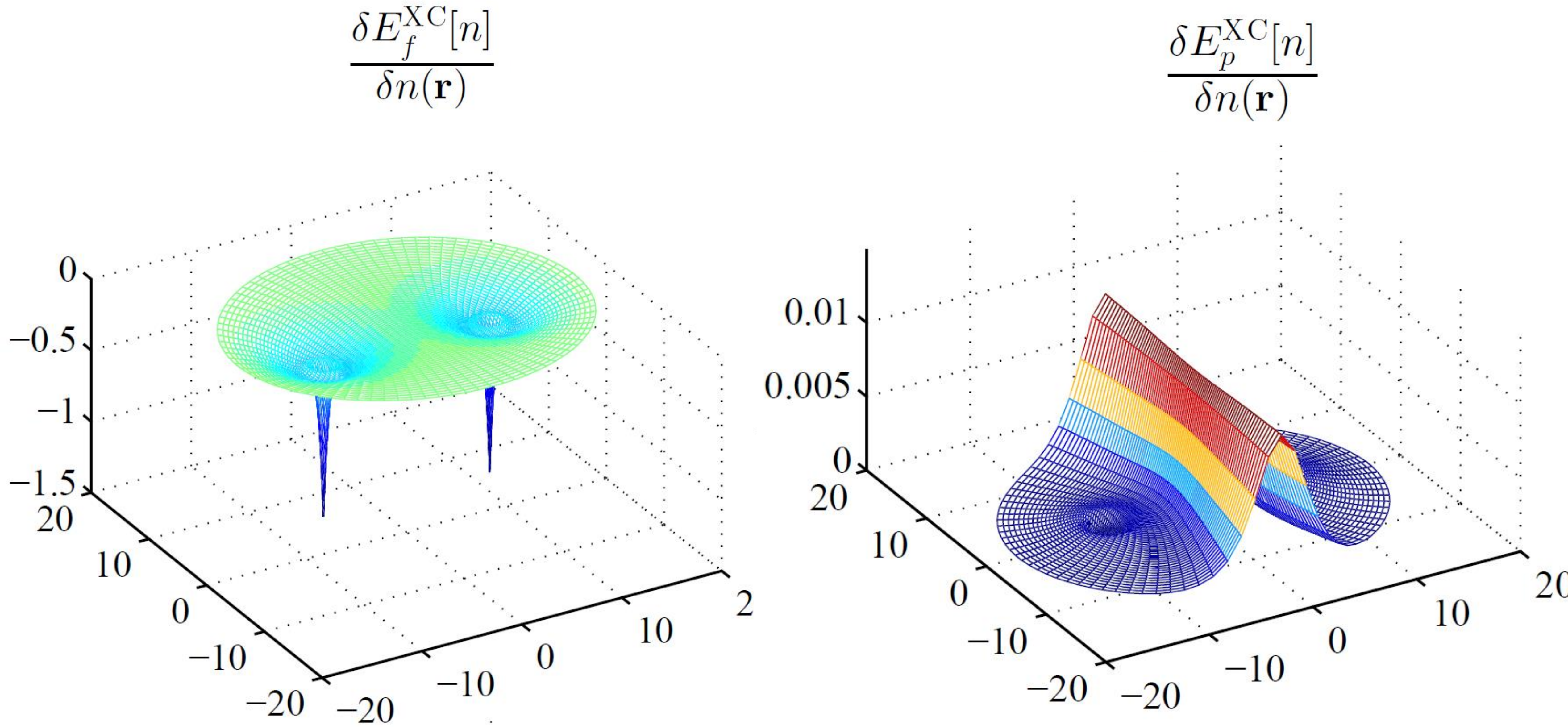
Li_2^+



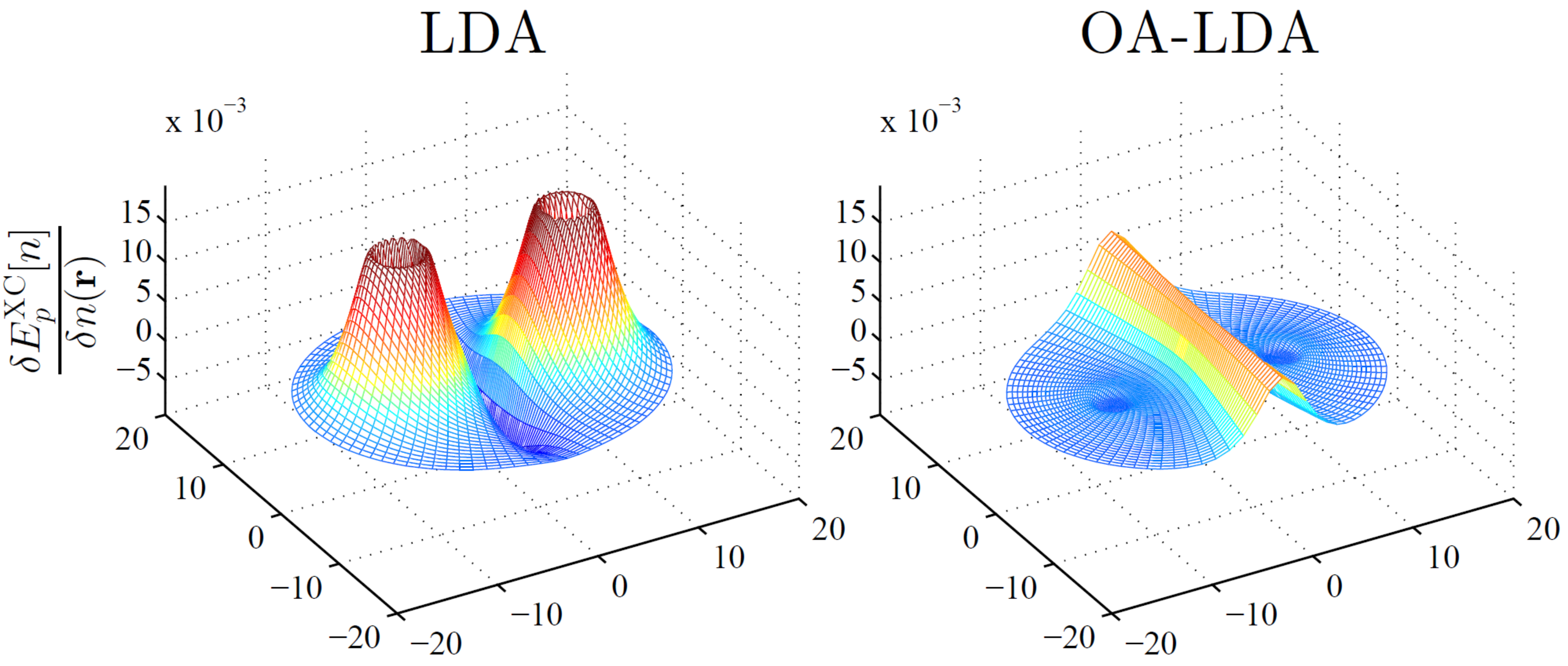


Solid lines:
without OA

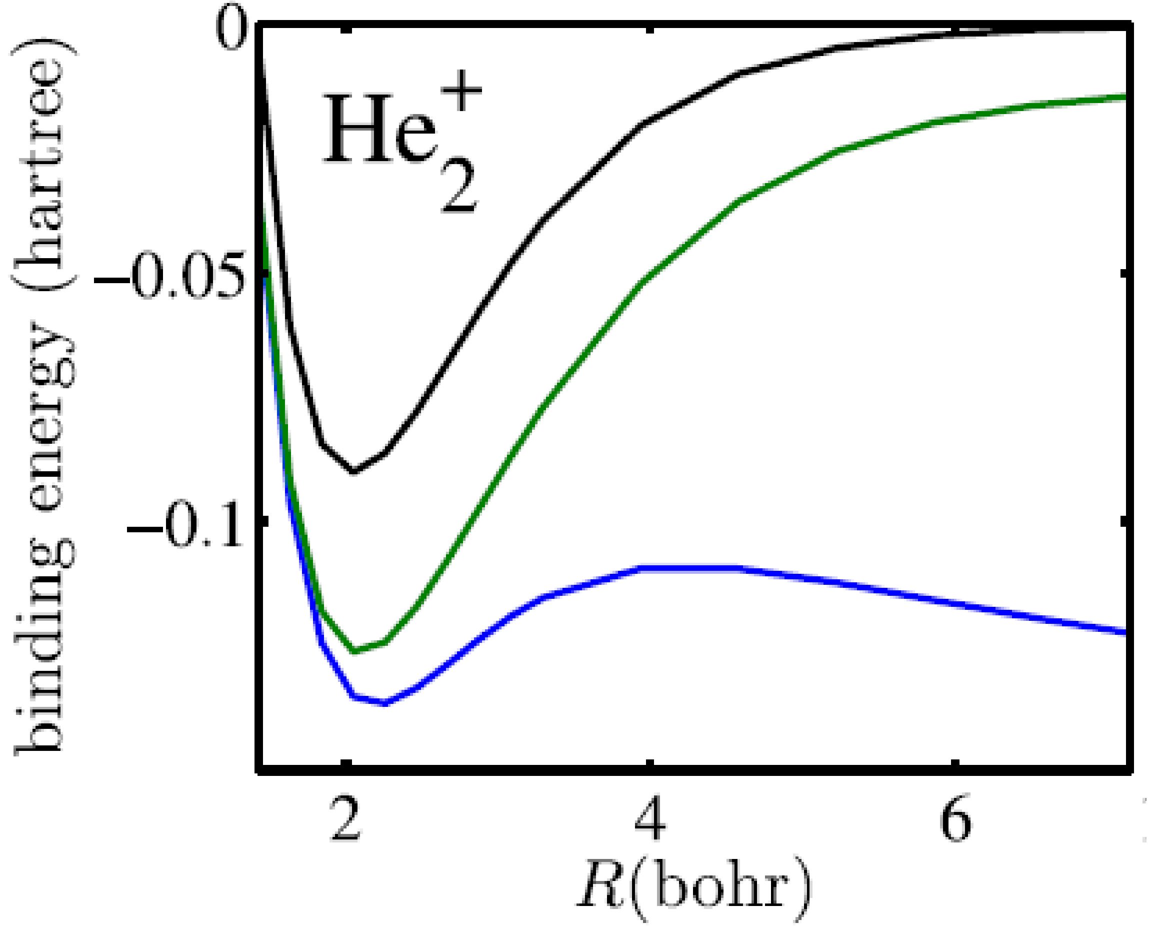
Dashed lines:
with OA



$\frac{\delta E_f^{\mathrm{XC}}[n]}{\delta n(\mathbf{r})}$
0
−0.5
−1
−1.5
20
10
0
−10
−20
−20
−10
0
10
2
$\frac{\delta E_p^{\mathrm{XC}}[n]}{\delta n(\mathbf{r})}$
0.01
0.005
0
20
10
0
−10
−20
−20
−10
0
10
20



LDA
OA-LDA
x 10^-3
x 10^-3
$\frac{\delta E_p^{\mathrm{XC}}[n]}{\delta n(\mathbf{r})}$
15
10
5
0
−5
20
10
0
−10
−20



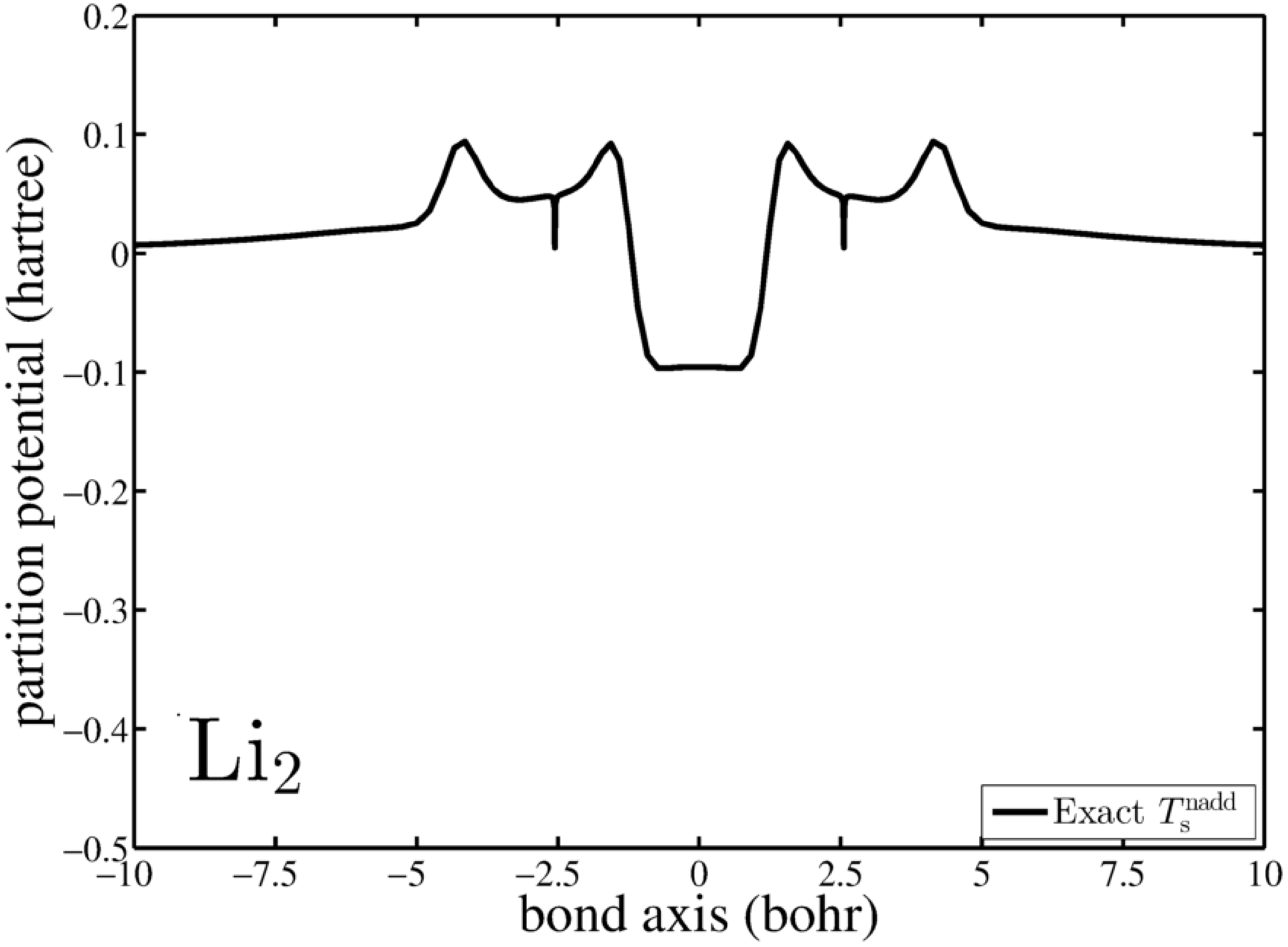
exact

LDA

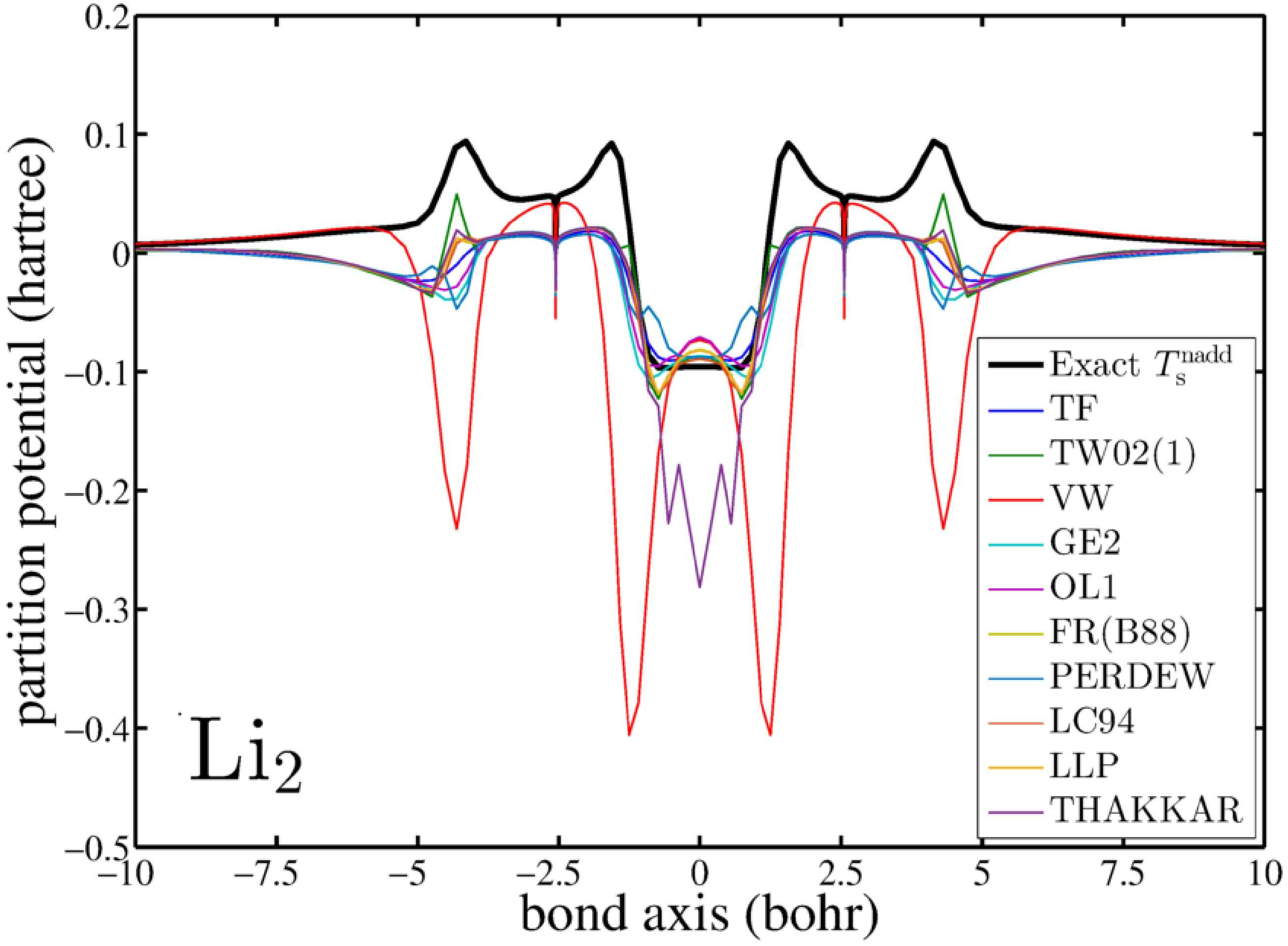
Approximate PDFT

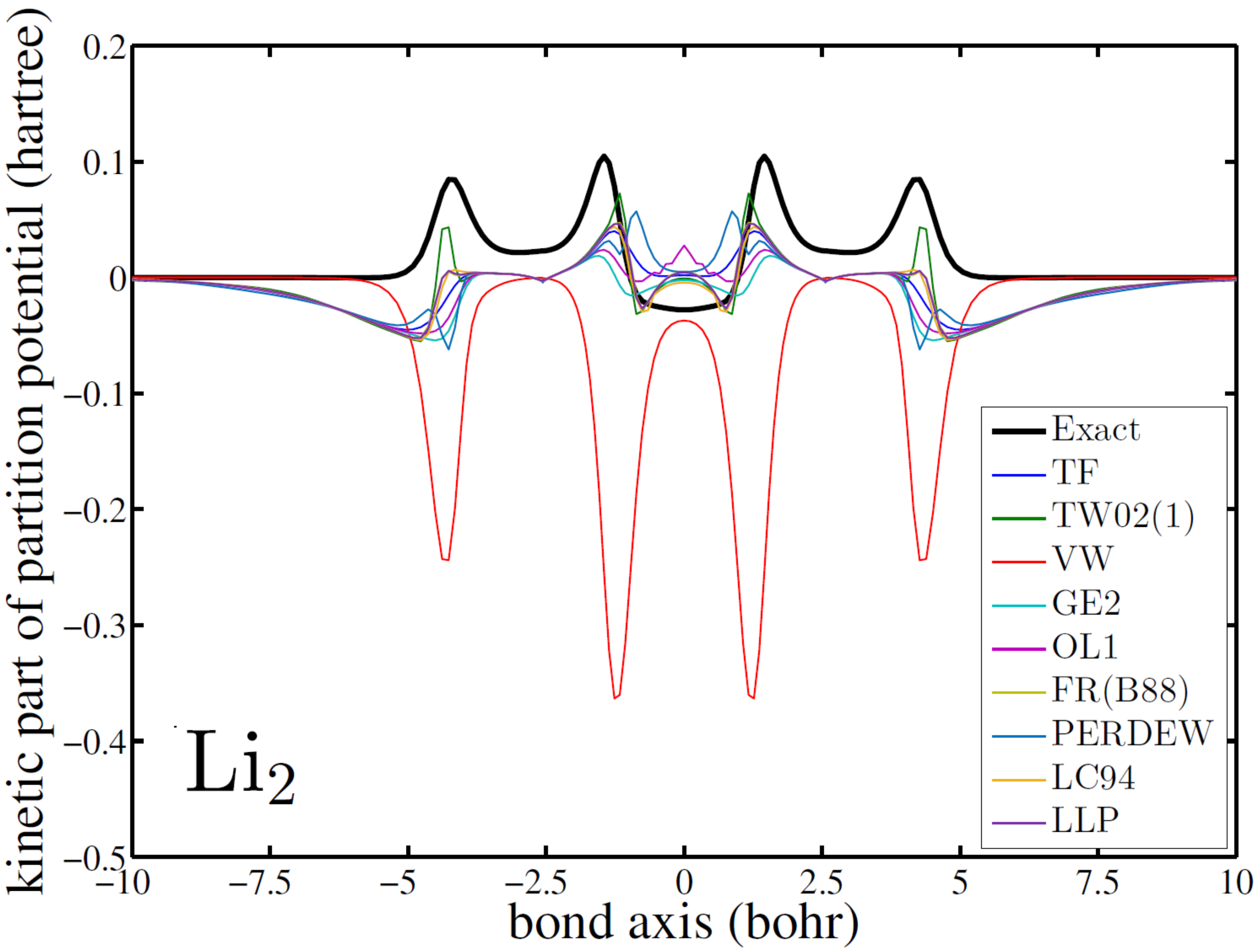
But inversions are expensive…

Partition potential along the bond axis



Partition potential along the bond axis




kinetic part of partition potential (hartree)
0.2
0.1
0
−0.1
−0.2
−0.3
−0.4
−0.5
−10
−7.5
−5
−2.5
0
2.5
5
7.5
10
bond axis (bohr)
Exact
TF
TW02(1)
VW
GE2
OL1
FR(B88)
PERDEW
LC94
LLP
Li2

T_s^{nad} at LDA Equilibrium for Li_2

Exact	TF	LP	APBE	TW02(1)
0.0048	-0.0080	-0.0088	-0.0072	-0.0073

VW	GE2	LIEB	ABSP1	GR
-0.2195	-0.0265	-0.0393	-0.2285	-0.2221

PEARSON	OL1	FR(B88)	FR(PW86)	PERDEW
-0.0085	-0.0197	-0.0097	-0.0082	-0.0086

VSK	VJKS	LC94	LLP	THAKKAR
-0.2296	0.0648	-0.0114	-0.0099	-0.0101

T_s^{nad} at LDA Equilibrium for Li_2

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VSK	**VJKS**	**LC94**	**LLP**	**THAKKAR**
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T_s^{nad} at LDA Equilibrium for Li_2

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VSK	**VJKS**	**LC94**	**LLP**	**THAKKAR**
-0.2296	0.0648	**-0.0114**	**-0.0099**	**-0.0101**

“Best” functional…

$$T_s^{\mathrm{nad}}[n] = 0$$

Re-parameterizing TW02

- TW02[5]

$$T_s[\rho] = \frac{3}{10}(3\pi^2)^{2/3}\int \rho^{5/3}(\mathbf{r})F_t(s(\mathbf{r}))\, d\mathbf{r}$$

$$F_t(s) = 1 + \kappa - \frac{\kappa}{1 + \frac{\mu}{\kappa}s^2}$$

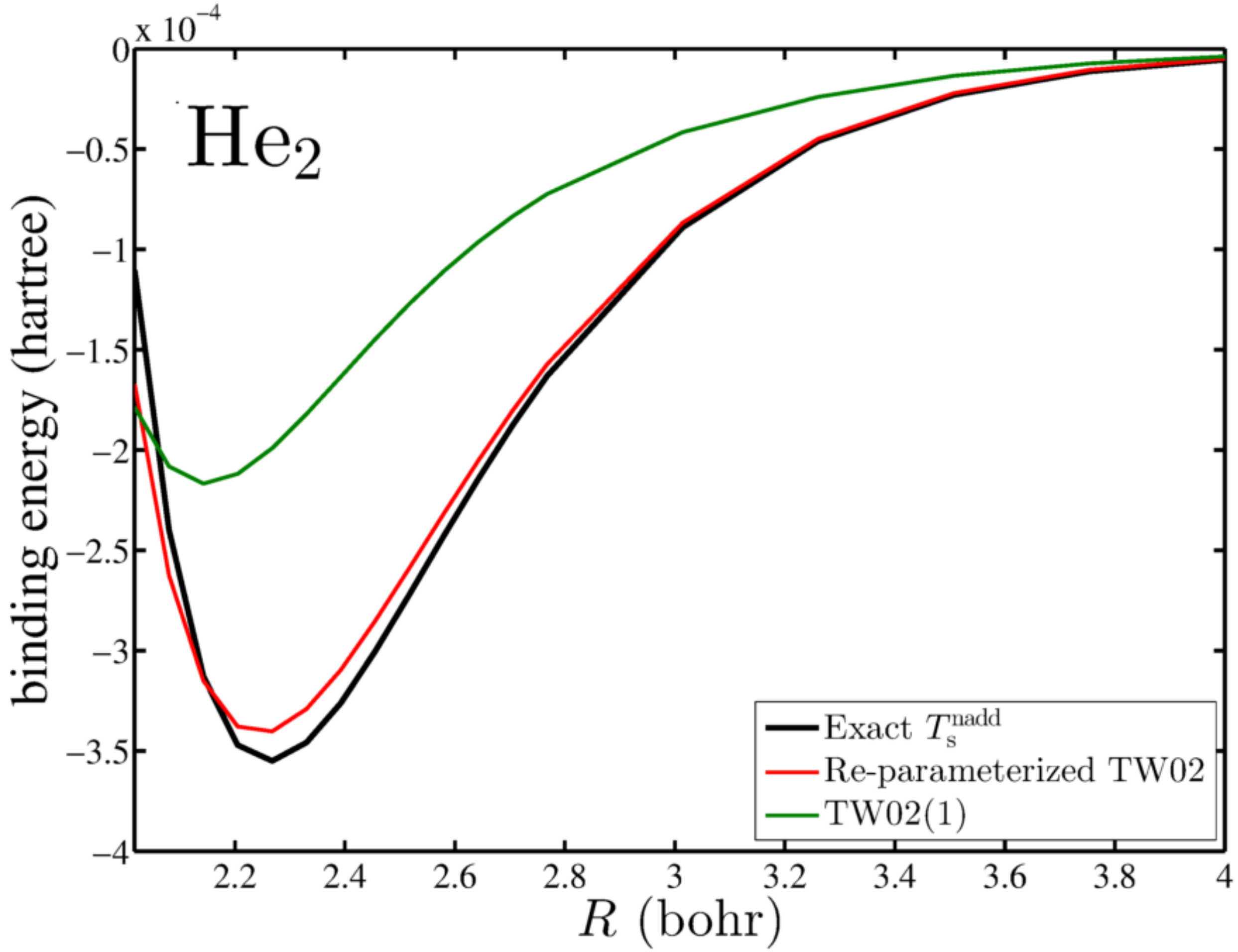
[5] F. Tran and T. A. Wesołowski, Int. J. Quantum Chem. **89**, 441 (2002).

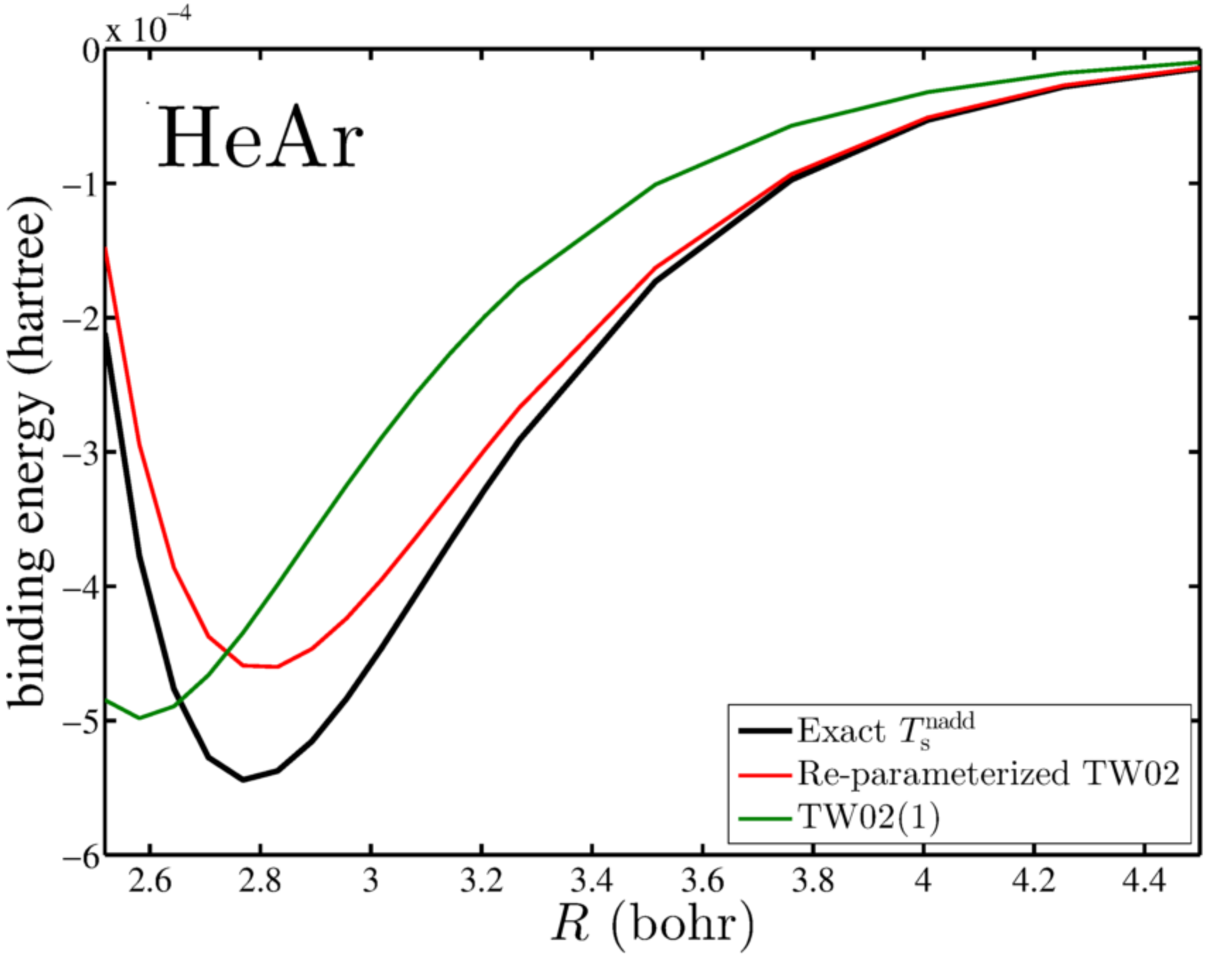
Re-parameterizing TW02

Functional	κ	μ
TW02(1)	0.8239	0.2335
TW02(2)	0.6774	0.2371
TW02(3)	0.8438	0.2319
TW02(4)	0.8589	0.2309
Re-parameterized TW02*	**1.9632**	**0.0198**

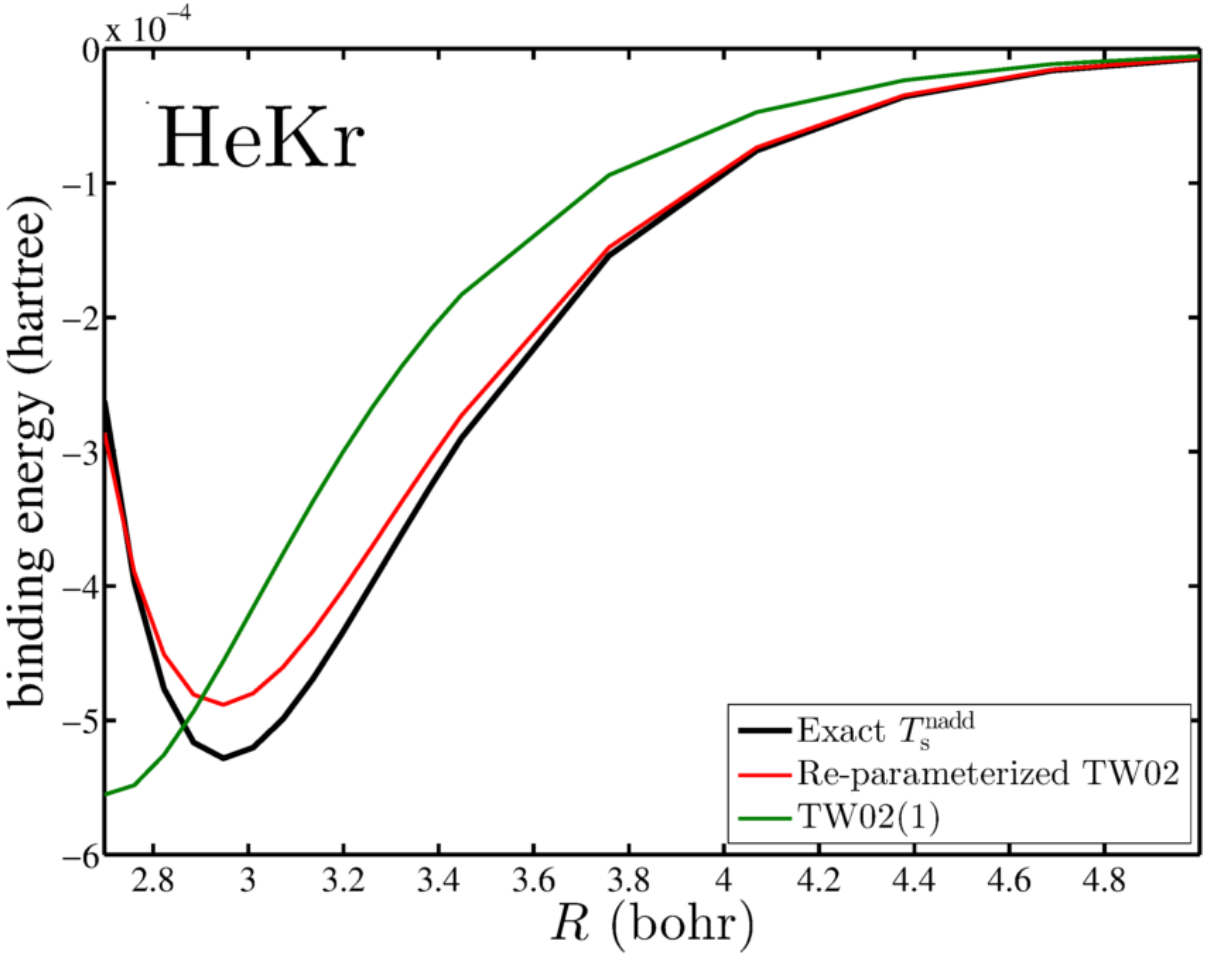
[5] F. Tran and T. A. Wesołowski, Int. J. Quantum Chem. **89**, 441 (2002).

* K. Jiang, J. Nafziger, and A. Wasserman, *to be published*.

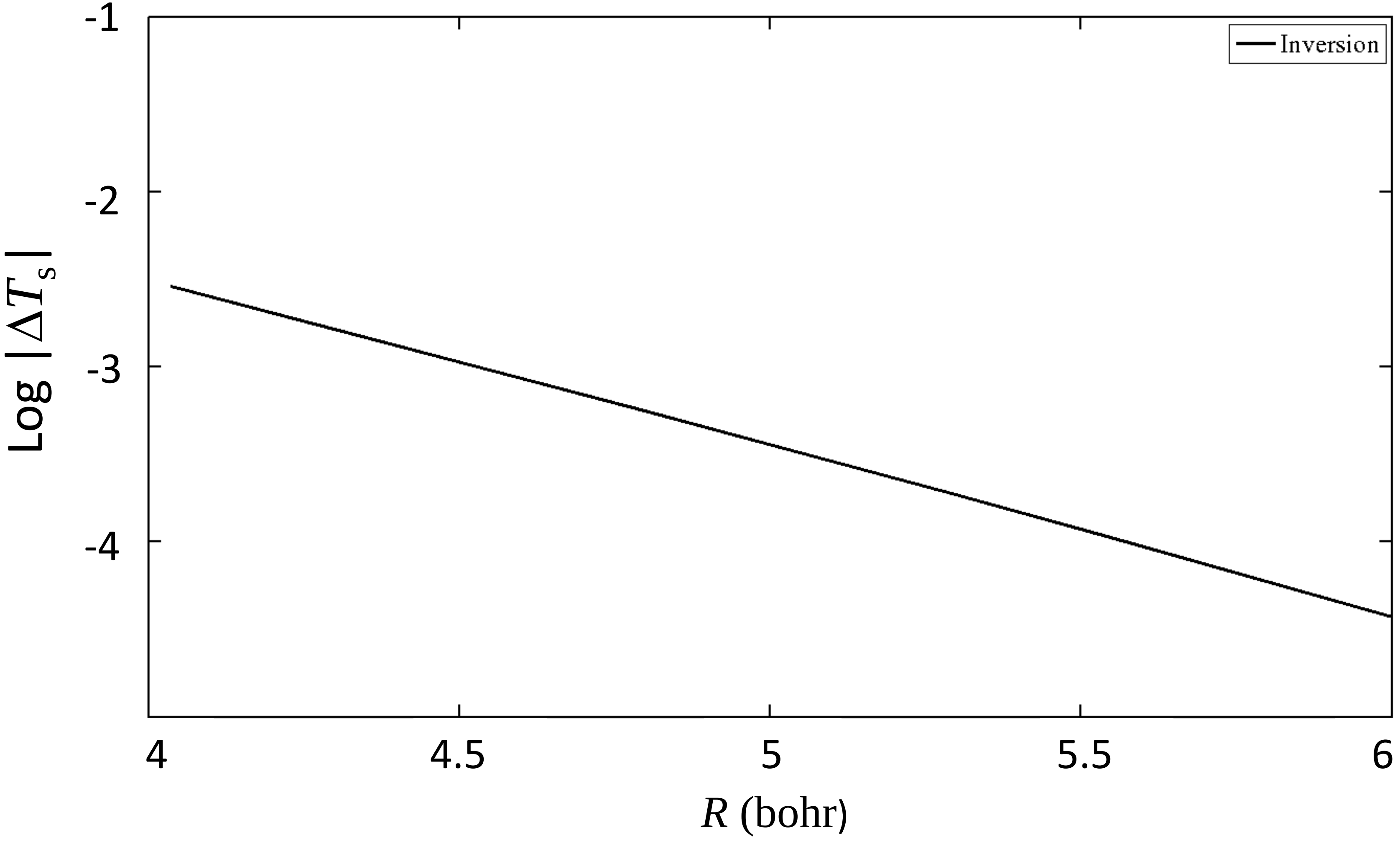

x 10^-4
He2
binding energy (hartree)
R (bohr)
Exact T_s^nadd
Re-parameterized TW02
TW02(1)
0
−0.5
−1
−1.5
−2
−2.5
−3
−3.5
−4
2.2
2.4
2.6
2.8
3
3.2
3.4
3.6
3.8
4



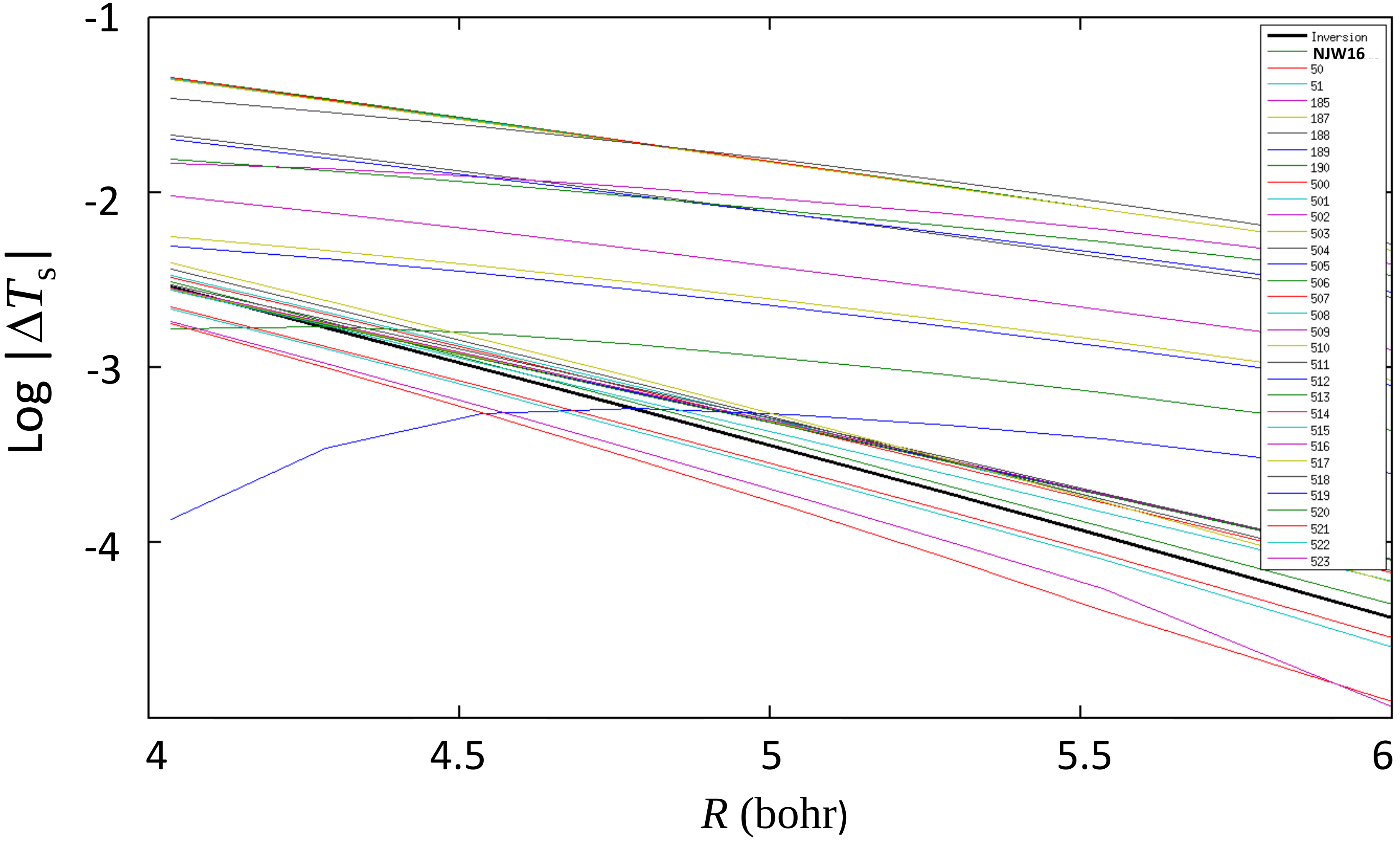
HeAr
x 10^−4
0
−1
−2
−3
−4
−5
−6
binding energy (hartree)
2.6
2.8
3
3.2
3.4
3.6
3.8
4
4.2
4.4
R (bohr)
Exact T_s^{nadd}
Re-parameterized TW02
TW02(1)


HeKr
x 10^−4
0
−1
−2
−3
−4
−5
−6
binding energy (hartree)
2.8
3
3.2
3.4
3.6
3.8
4
4.2
4.4
4.6
4.8
R (bohr)
Exact T_s^{nadd}
Re-parameterized TW02
TW02(1)

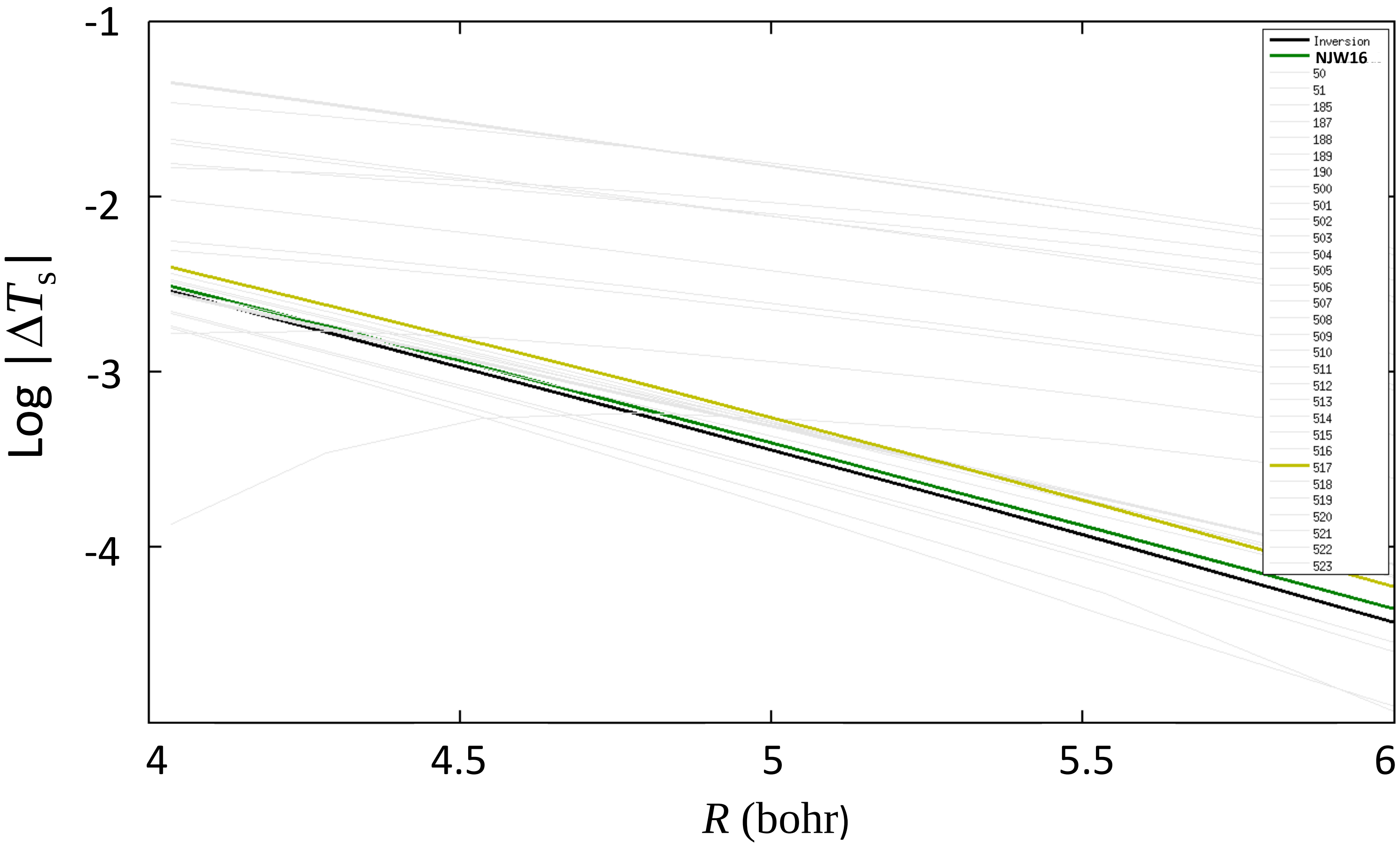
He_2 - LDA



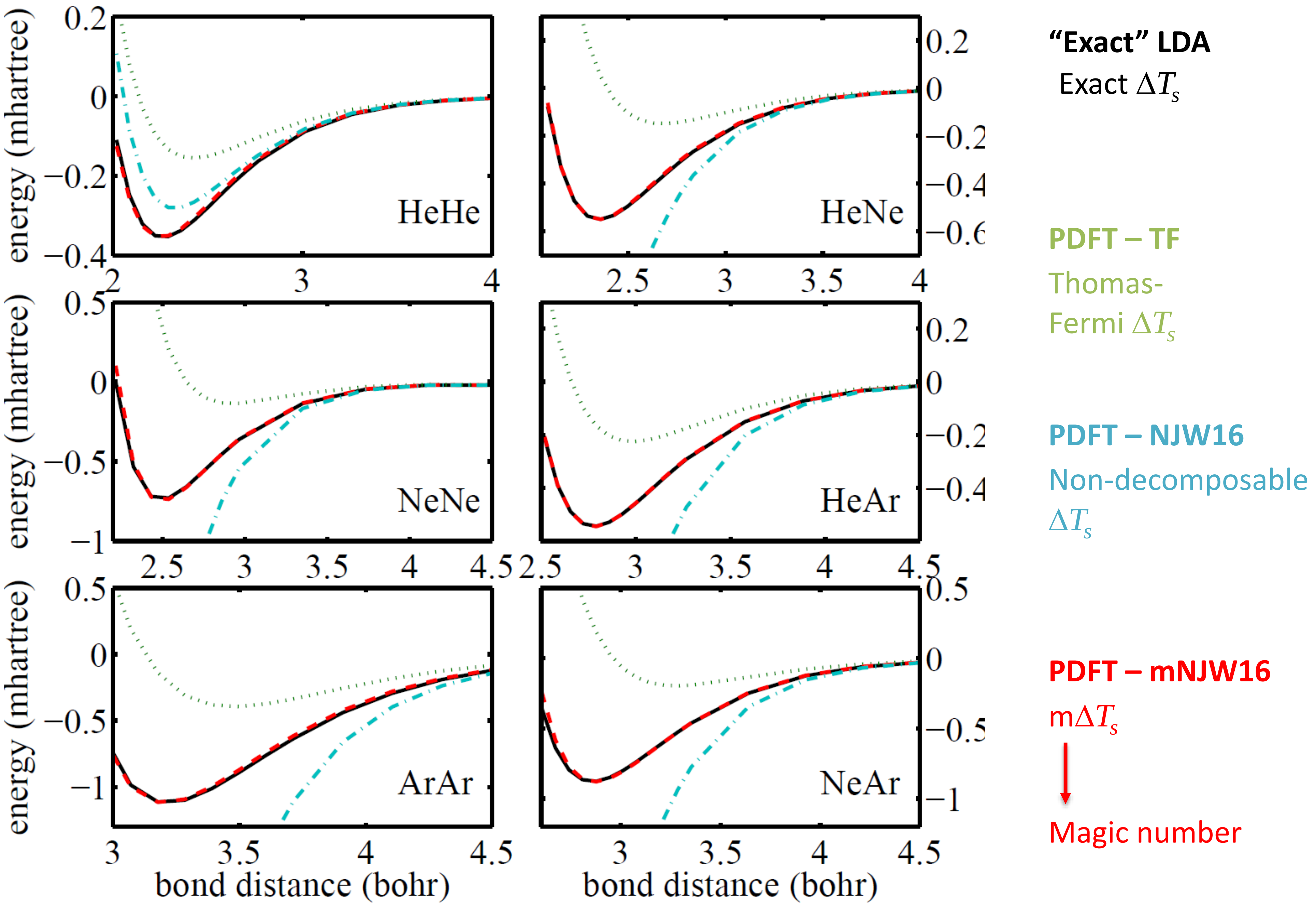
He_2 - LDA


Log |ΔT_s|
-1
-2
-3
-4
4
4.5
5
5.5
6
R (bohr)
Inversion
NJW16
50
51
185
187
188
189
190
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523

He_2 - LDA



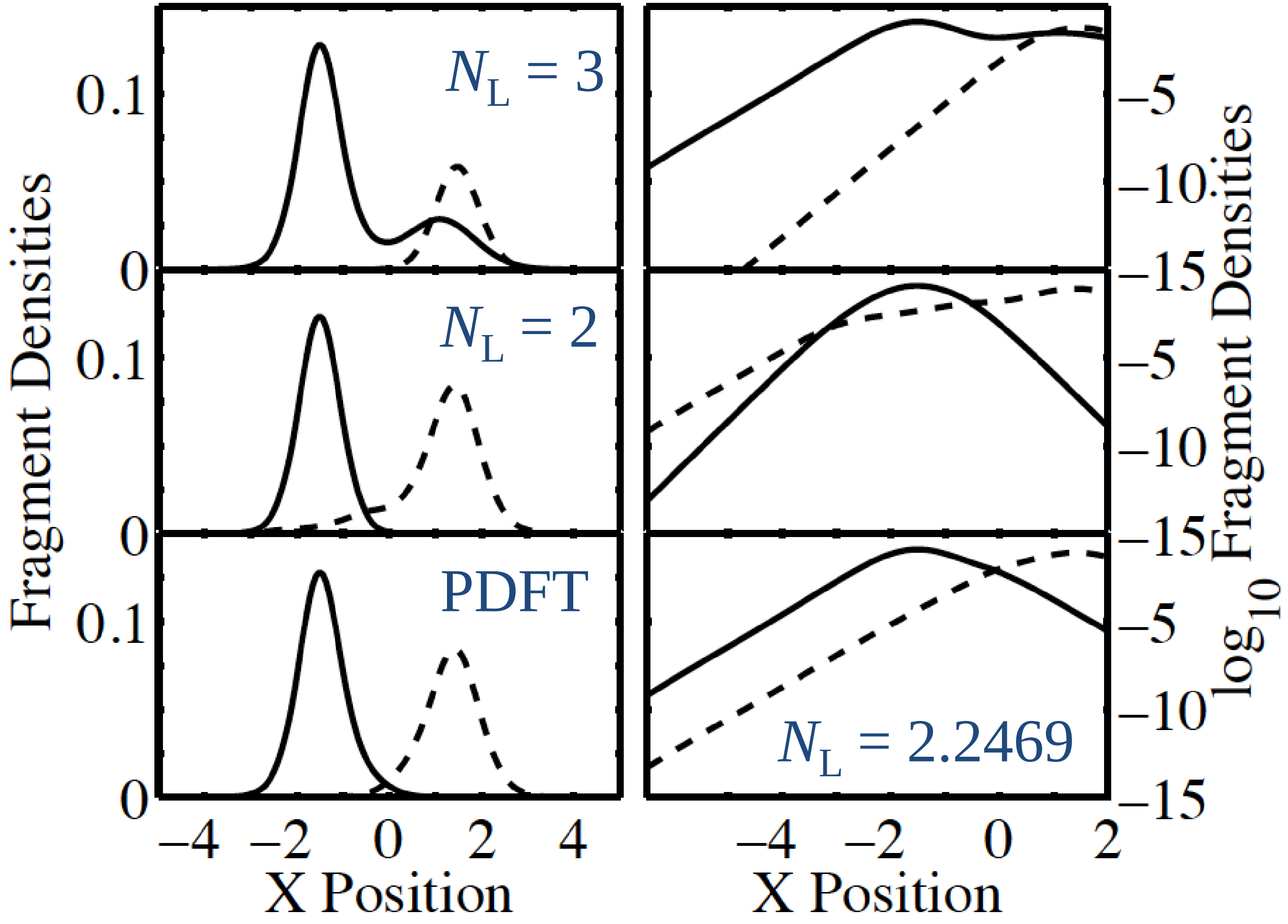
Only two are magic-numberable: NWJ16, and Perdew's GGA for $T_s[n]$



energy (mhartree)
bond distance (bohr)
HeHe
HeNe
NeNe
HeAr
ArAr
NeAr
"Exact" LDA
Exact ΔT_s
PDFT – TF
Thomas-Fermi ΔT_s
PDFT – NJW16
Non-decomposable ΔT_s
PDFT – mNJW16
mΔT_s
Magic number

Occupation Number Optimization

$$0 = \frac{\partial G}{\partial \nu_\alpha} = \mu_\alpha - \mu_m$$



Double-well 1D-potential with 4 non-interacting electrons.

Partition Density Functional Theory

Constrained minimization of:

$$E_f[\{n_\alpha\}] \equiv \sum_\alpha E_\alpha[n_\alpha]$$

where:

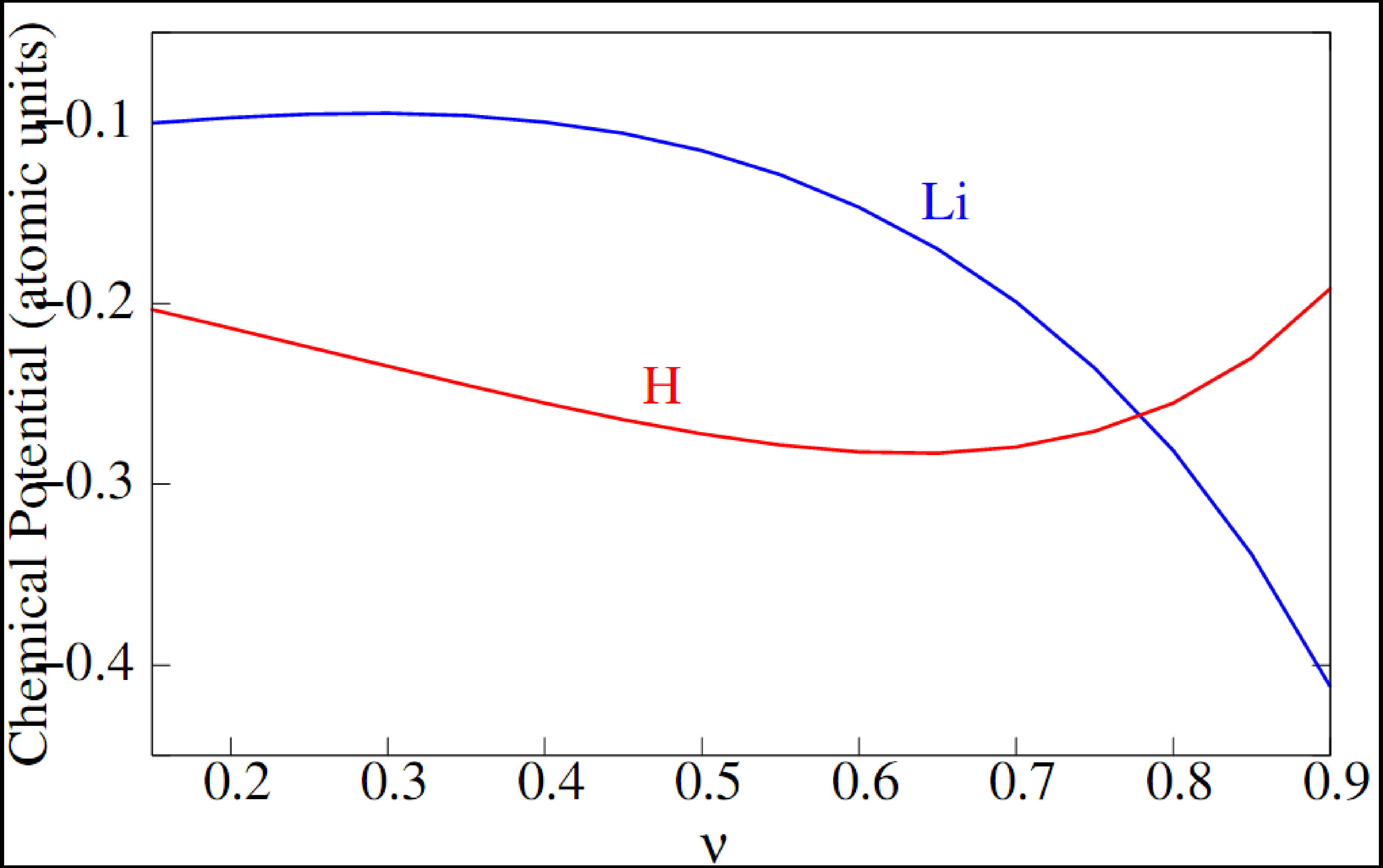
$$E_\alpha[n_\alpha] = \nu_\alpha E_{v_\alpha}[n_{p_\alpha+1}] + (1-\nu_\alpha) E_{v_\alpha}[n_{p_\alpha}]$$

$$G[\{n_\alpha\}] = E_f[\{n_\alpha\}] + \int v_p(\mathbf{r})\,(n_f(\mathbf{r}) - n(\mathbf{r}))\,d\mathbf{r} - \mu_m \left(\int n_f(\mathbf{r}) d\mathbf{r} - N \right)$$

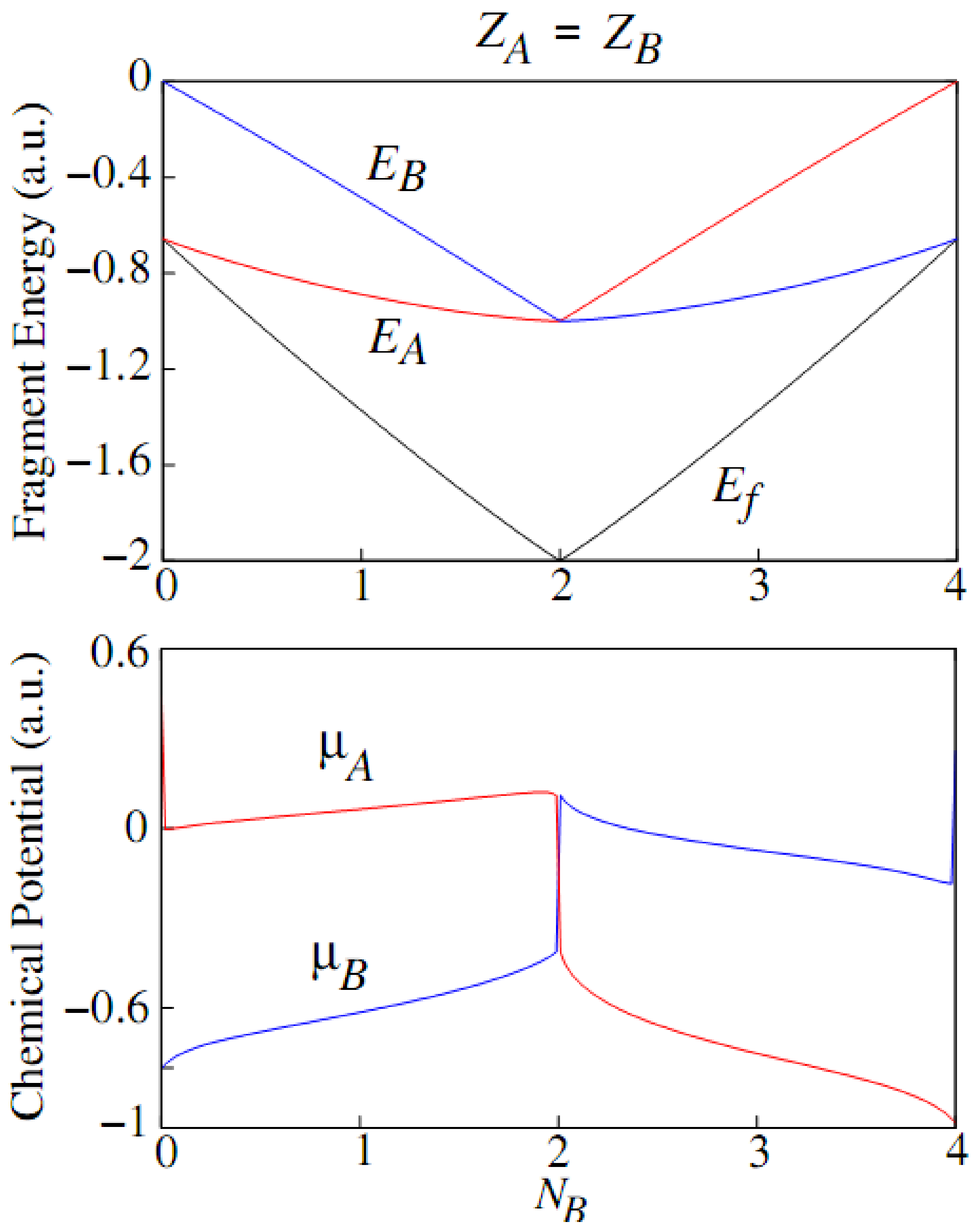
M.H. Cohen and A. Wasserman, JPCA **111**, 2229 (2007).

P. Elliott, K. Burke, M.H. Cohen and A. Wasserman, Phys. Rev. A **82**, 024501 (2010).

Lithium Hydride



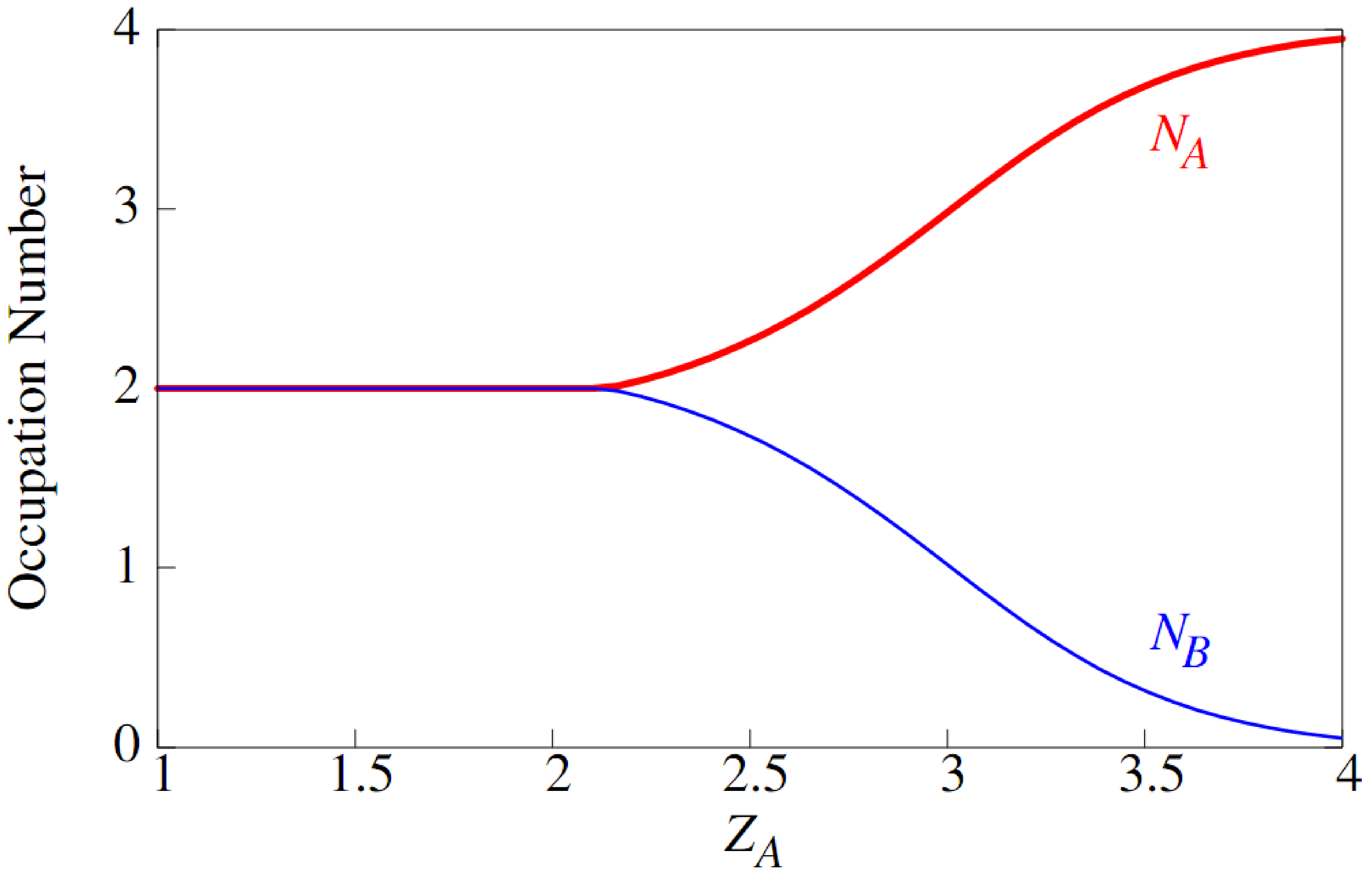
B3LYP / aug-cc-pVQZ



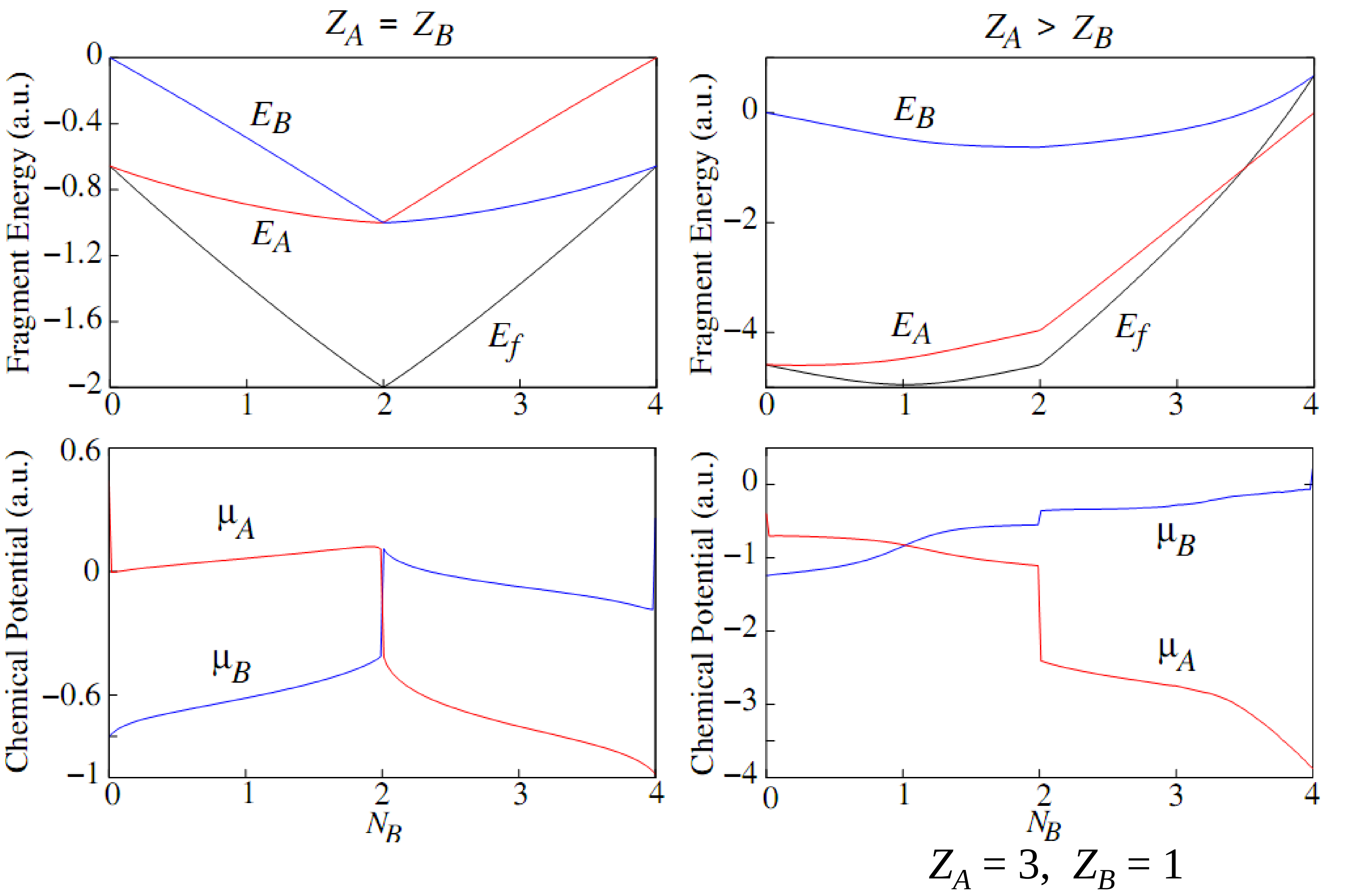
$$v(x) = -Z_A \cosh^{-2}(x-a) - Z_B \cosh^{-2}(x+a)$$

4 non-interacting “electrons”

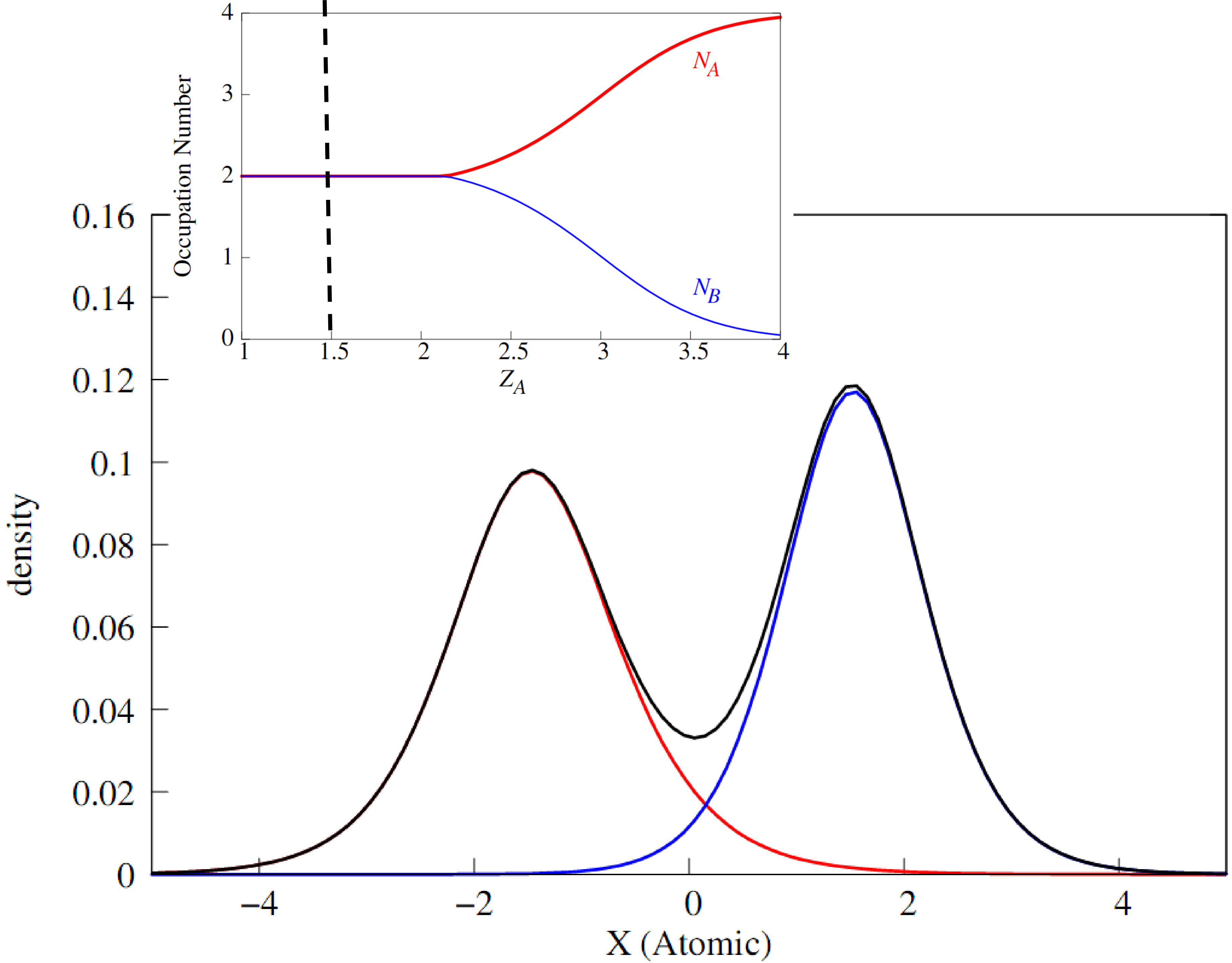
R. Tang, J. Nafziger, and A. Wasserman, Phys. Chem. Chem. Phys. **14**, 7880 (2012).



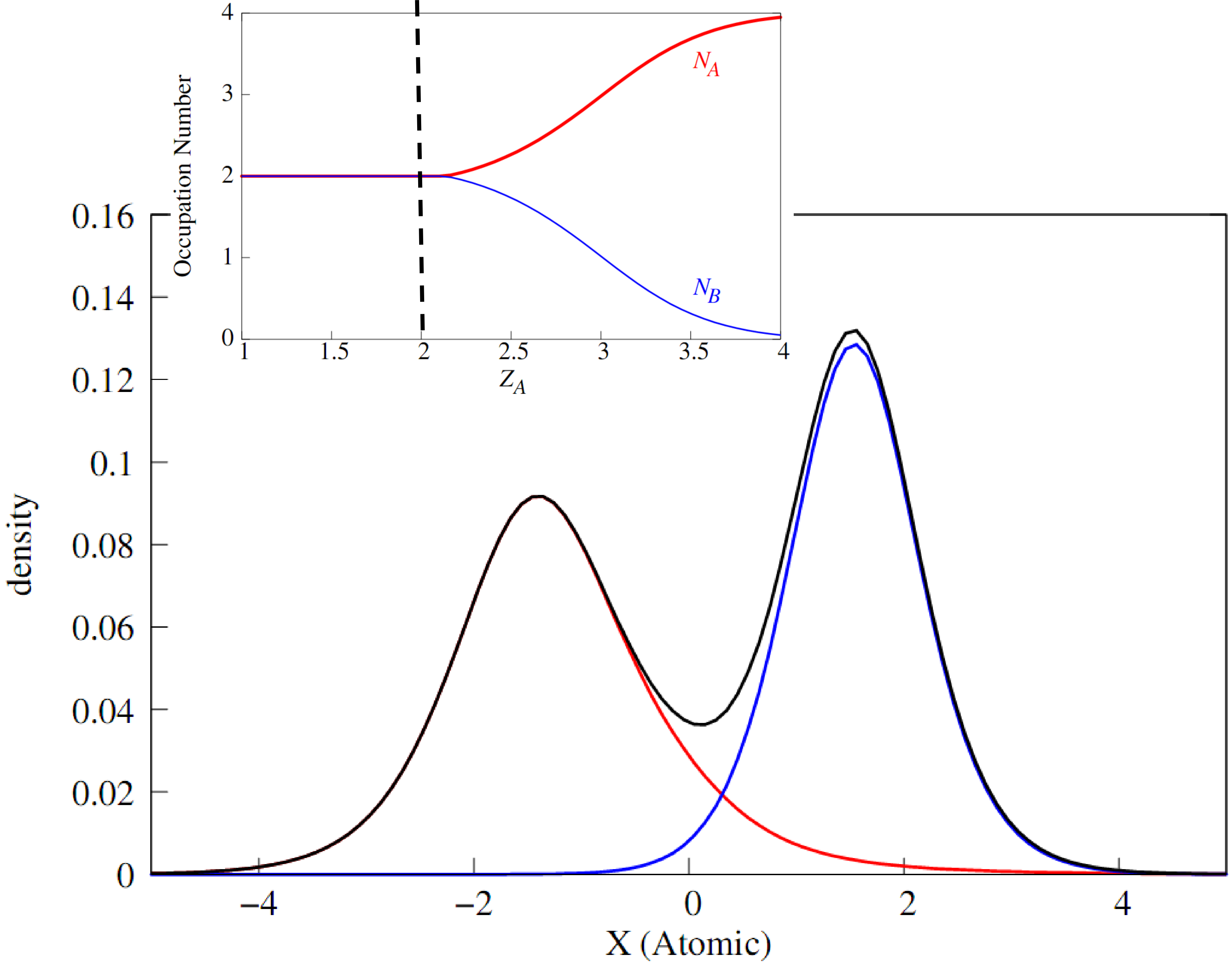
Fixed Z_B = 1

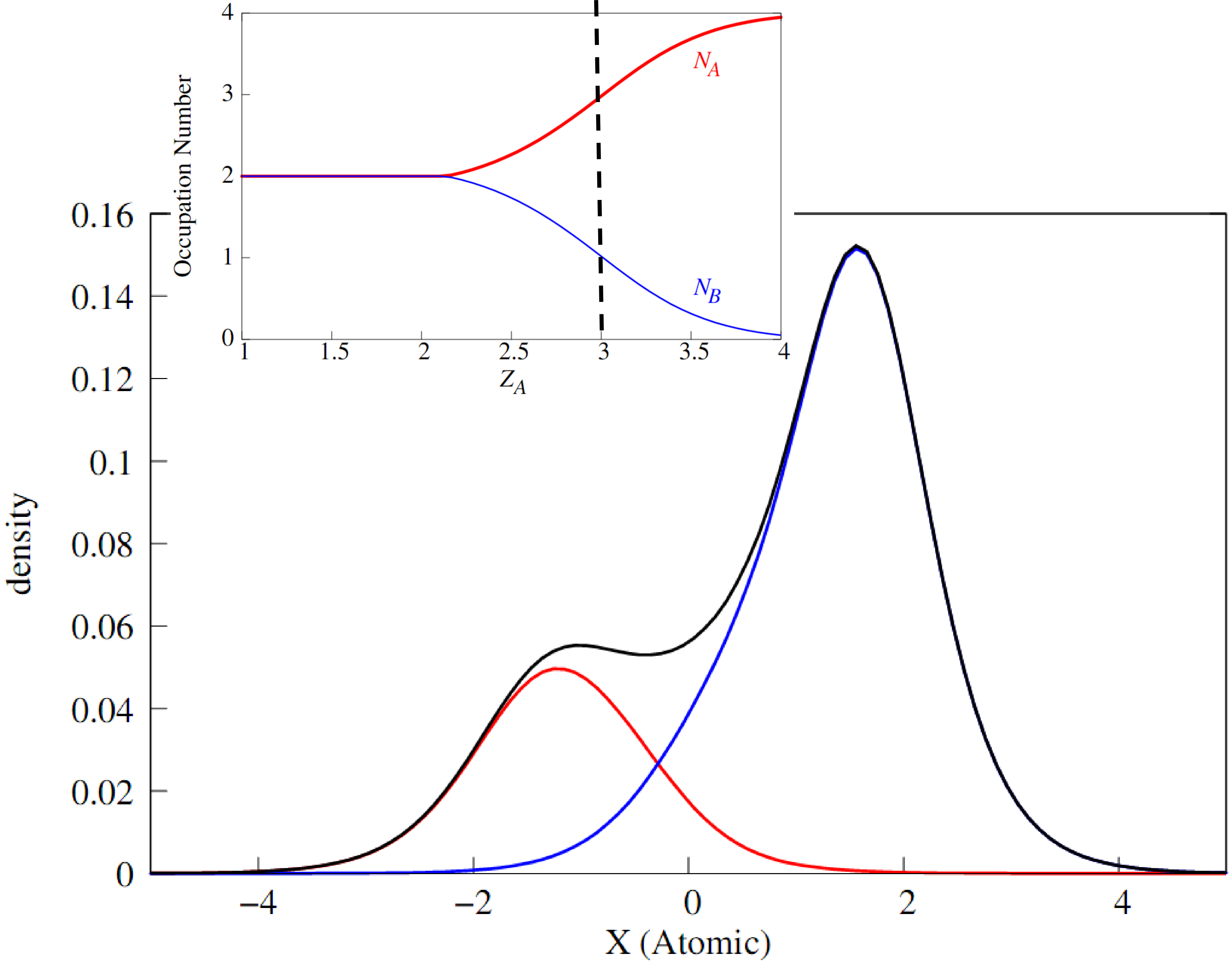


Z_A = Z_B
Z_A > Z_B
Fragment Energy (a.u.)
E_B
E_A
E_f
Chemical Potential (a.u.)
μ_A
μ_B
N_B
Z_A = 3, Z_B = 1



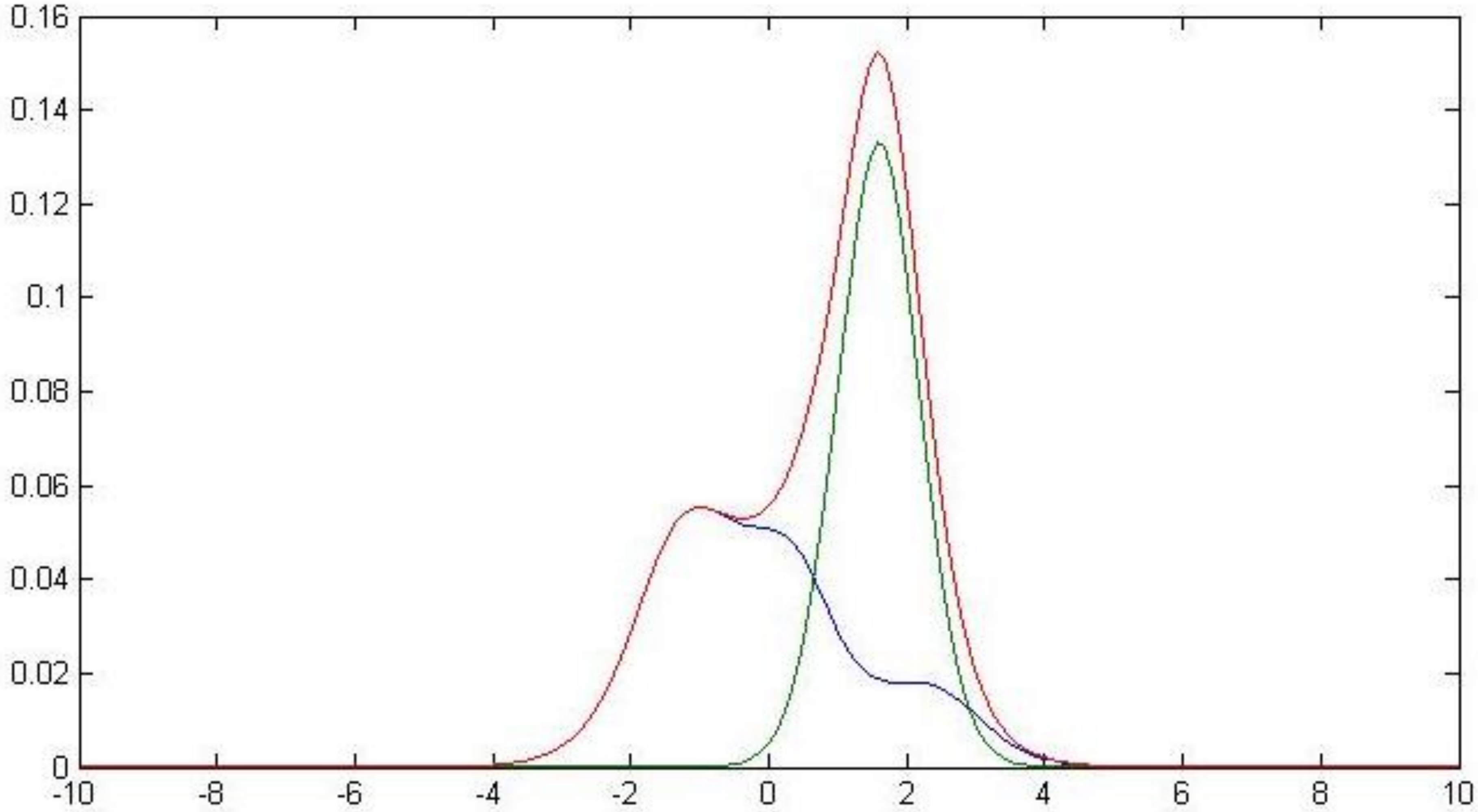
Occupation Number
N_A
N_B
Z_A
0
1
2
3
4
1
1.5
2
2.5
3
3.5
4
density
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
−4
−2
0
2
4
X (Atomic)


Occupation Number
N_A
N_B
Z_A
density
X (Atomic)

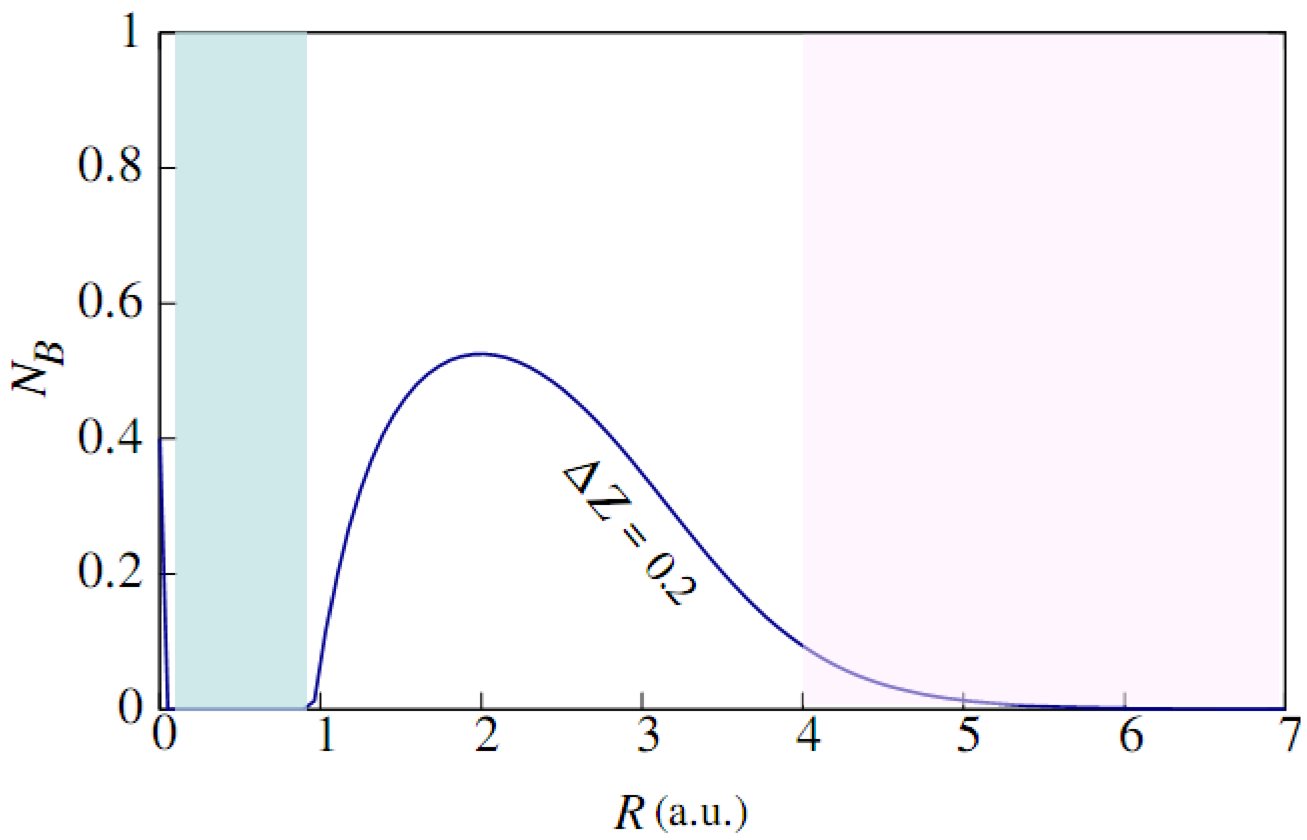


Occupation Number
Z_A
N_A
N_B
density
X (Atomic)

Forcing occupation numbers to integers:

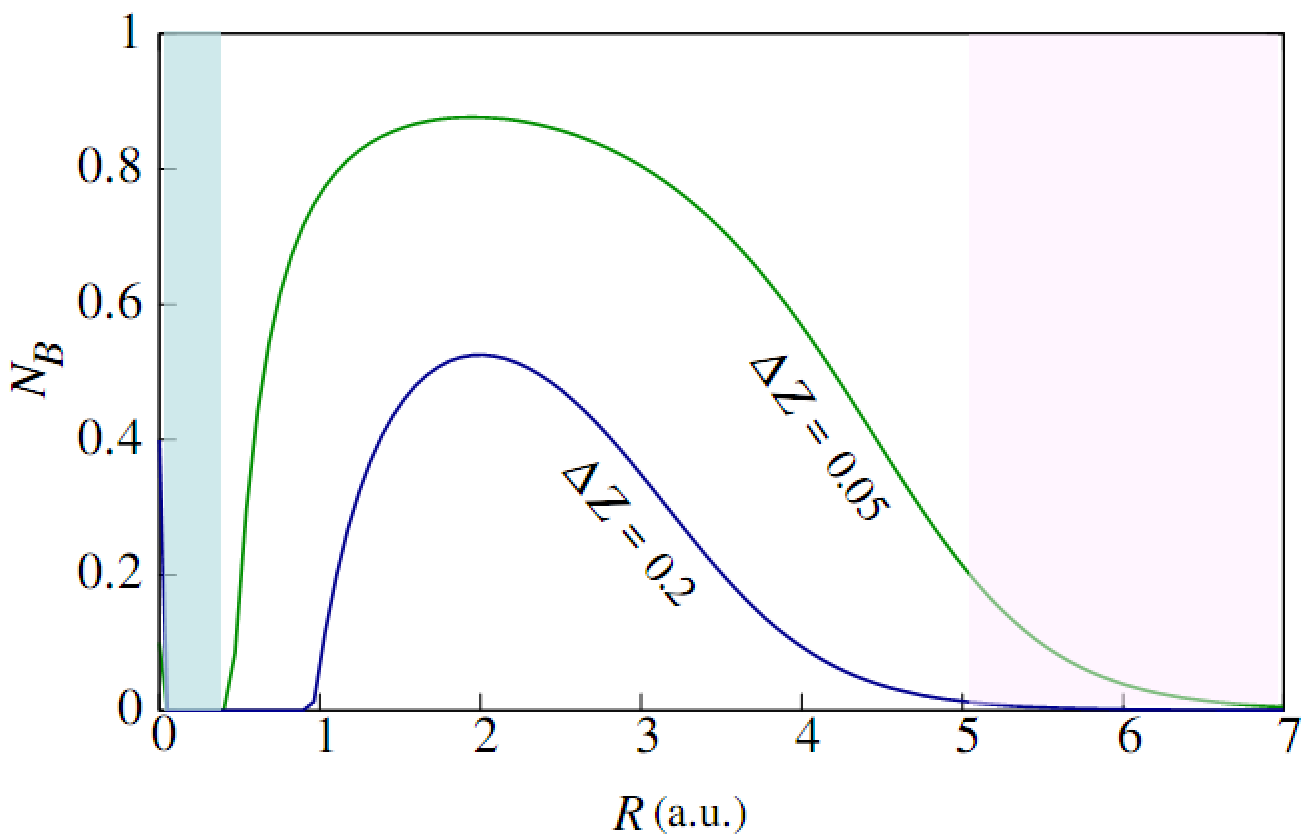


Small separations lead to integer occupations



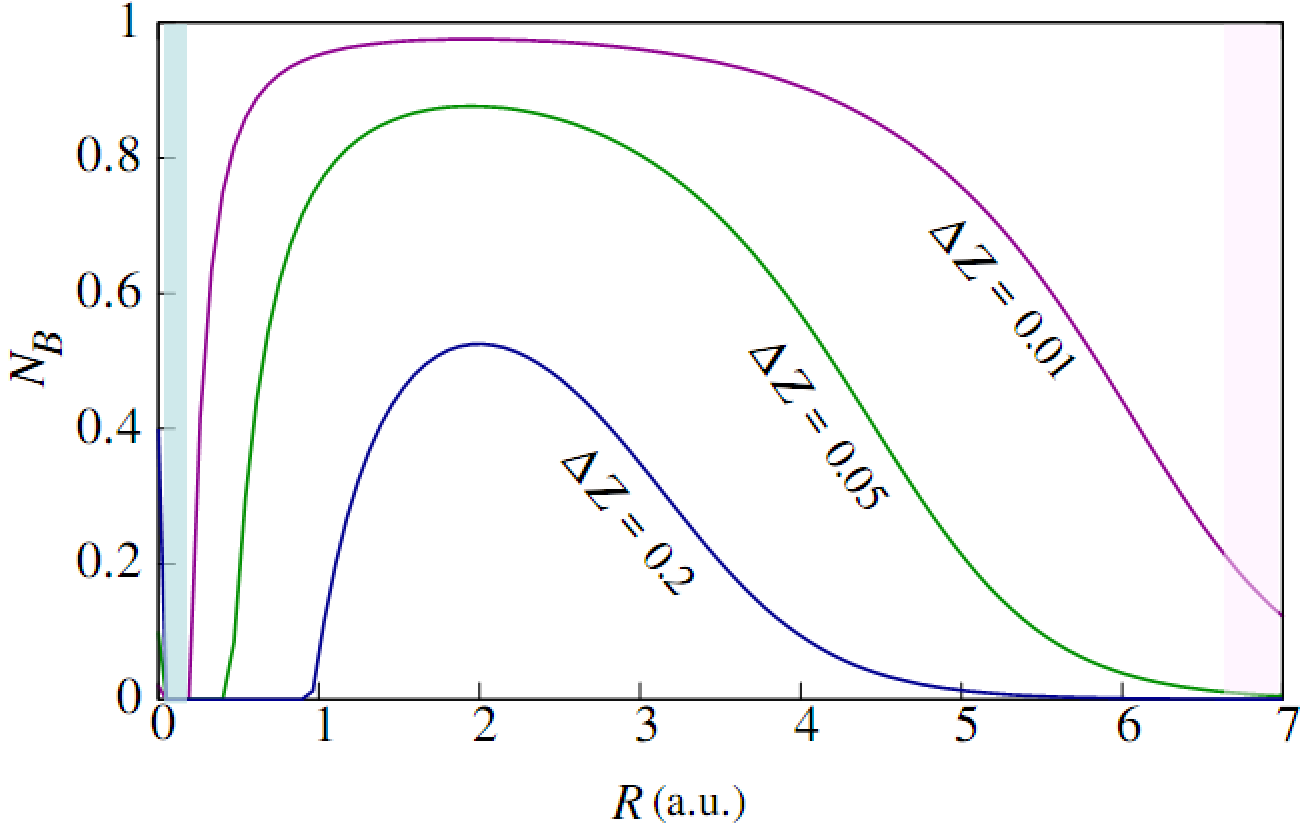
Large separations lead to near-integer occupations

Small separations lead to integer occupations



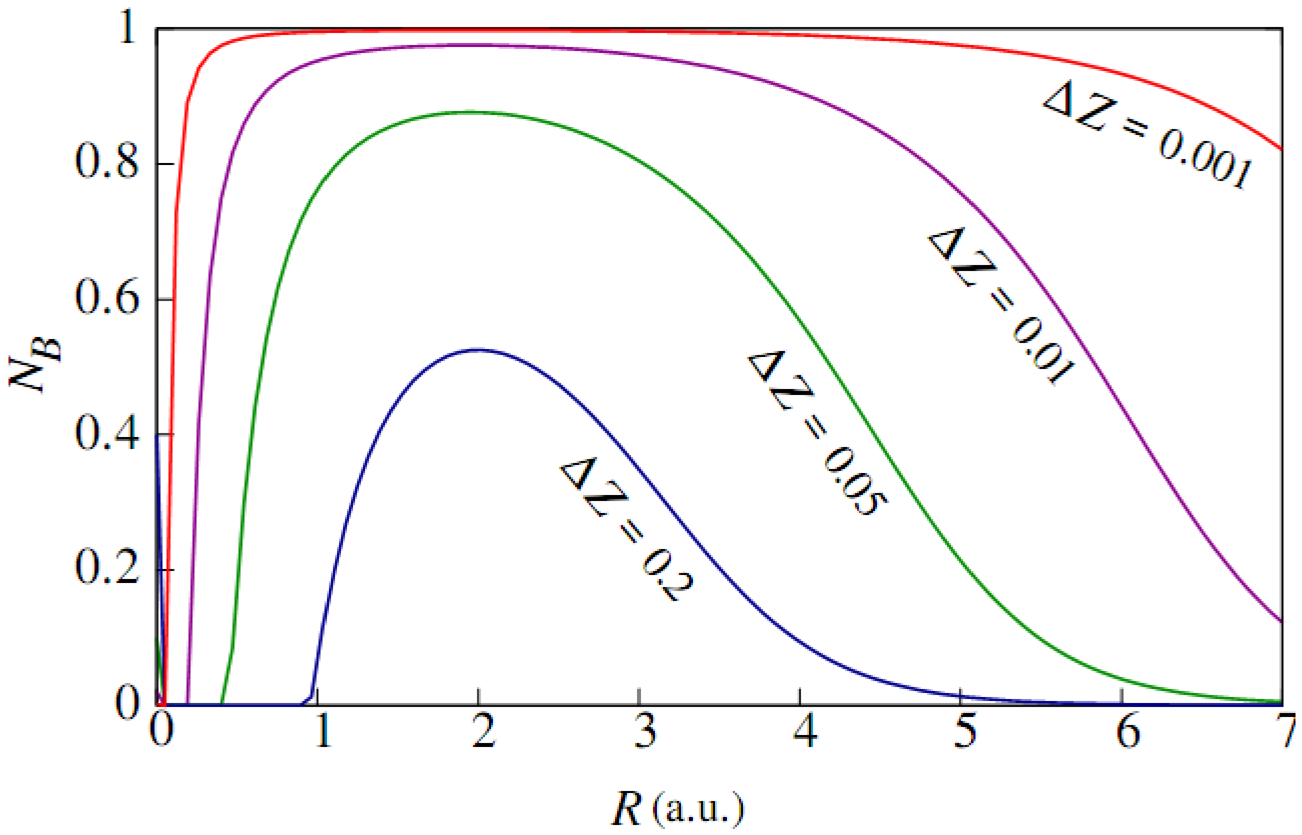
Large separations lead to near-integer occupations

Small separations lead to integer occupations



Large separations lead to near-integer occupations

Small separations lead to integer occupations



Large separations lead to near-integer occupations

Main conclusion

$$E = E_p + E_f$$

$$E_p[\{n_{i\alpha\sigma}\}] = T_s^{\text{nad}} + E_{\text{H}}^{\text{nad}} + E_{\text{xc}}^{\text{nad}} + V_{\text{ext}}^{\text{nad}}$$

inter-fragment interactions

$$E_f = \sum_\alpha E_\alpha[n_\alpha]$$

intra-fragment interactions

An alternative to developing more sophisticated XC-functionals (to be used in standard KS-DFT) is to develop simple E_p- functionals (to be used in PDFT).

Thanks to:

Jonathan Nafziger, Kaili Jiang

NSF, DOE