Introduction to Ground State Density Functional Theory
Part II

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TDDFT School, Rutgers – Newark, June 30, 2023

Eleven references for basics of ground-state DFT

1. K. Burke, *ABC of DFT* ; http://dft.uci.edu
2. J.P. Perdew and S. Kurth, *Density Functionals for Non-relativistic Coulomb Systems in the New Century,* in *A Primer in Density Functional Theory*, edited by C. Fiolhais et al. (Springer-Verlag, NY, 2003).
3. R.M. Dreizler and E.K.U. Gross, *Density Functional Theory* (Springer-Verlag, Berlin, 1990).
4. R. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford, New York, 1989).
5. J.P. Perdew, *What do the Kohn-Sham energies mean? How do atoms dissociate?*, in NATO ASI Ser., Ser.B 123 (Density Funct. Methods Phys.), 265 (1985).
6. G.F. Giuliani and G. Vignale, Chapter 7 in *Quantum Theory of the Electron Liquid*, (Cambridge University Press, 2005).
7. E.J. Baerends, O.V. Gritsenko, and R. van Meer, *Perspective: The Kohn-Sham gap, the fundamental gap, and the optical gap: the physical meaning of occupied and virtual Kohn-Sham orbital energies*, Phys. Chem. Chem. Phys. **15**, 16408 (2013).
8. E.J. Baerends, *Chemical Potential, etc.* Phys. Chem. Chem. Phys. **24**, 12745 (2022).
9. A. Ruzsinsky and J.P. Perdew, *Twelve outstanding problems in ground-state density functional theory: A bouquet of puzzles*, Comp. Theor. Chem. **963**, 2 (2011).
10. A.J. Cohen, P. Mori-Sanchez, and W. Yang, *Challenges for Density Functional Theory*, Chem. Rev. **112**, 289 (2012).
11. A. Wasserman, J. Nafziger, K. Jiang, M-C.Kim, E. Sim, and K. Burke, *The Importance of Being Inconsistent*, Ann. Rev. Phys. Chem. **68**, 555 (2017).

Outline

<u>Method for this lecture</u>: Go back to the basics from yesterday and discuss selected FAQ and FHM

- Simple examples of density functionals
- Chemical Potential
- Derivative Discontinuities
- Key errors (self-interaction, delocalization, static-correlation)

Real system	Fictitious system

$$I = I_s$$

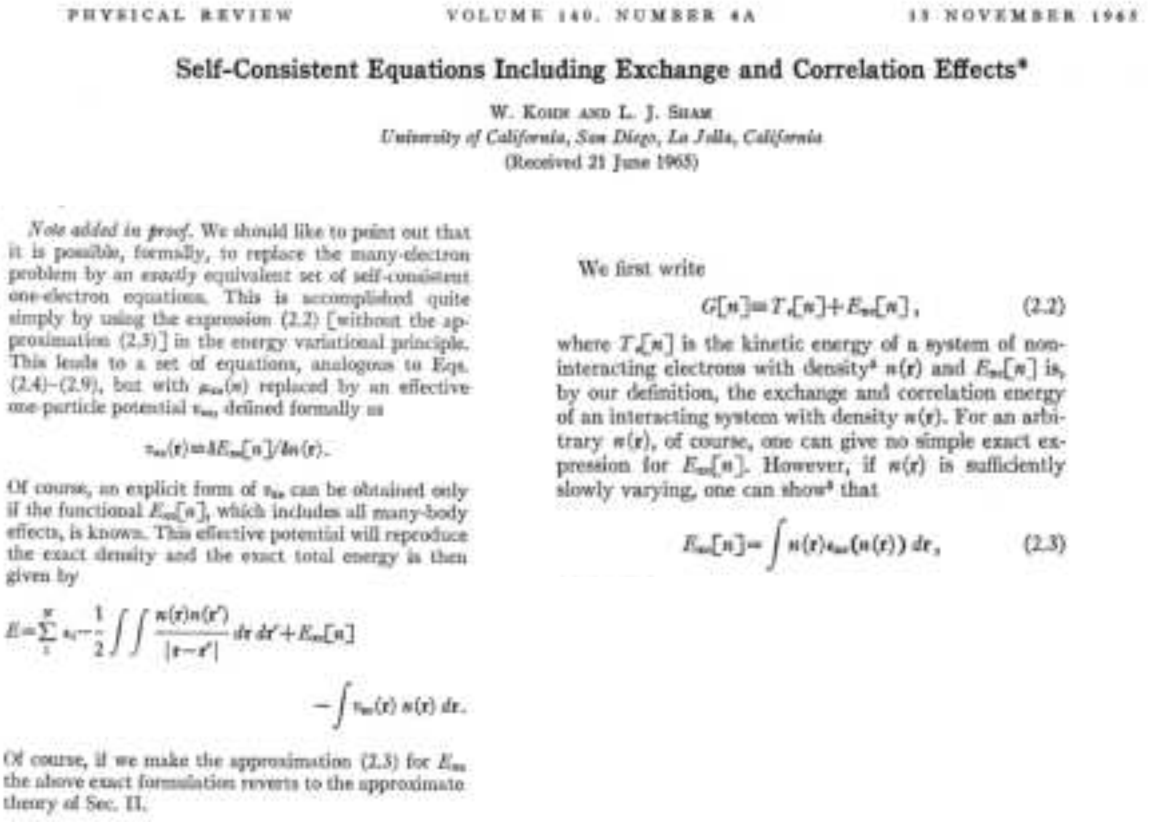
$$N \int dx_2 \ldots \int dx_N \, |\Psi_0|^2 = n(\mathbf{r}) = \sum_i |\phi_i|^2$$

$$\left(-\frac{1}{2}\nabla^2 + v_s(\vec{r})\right)\phi_i = \varepsilon_i \phi_i$$

$$\downarrow$$

$$v(\vec{r}) + v_H(\vec{r}) + v_{xc}(\vec{r})$$

$$E = E_s + E_{Hxc} - \int d\vec{r}\, v_{Hxc}(\vec{r})\, n(\vec{r}) \qquad E_s = \sum_{i,occ} \varepsilon_i$$



PHYSICAL REVIEW VOLUME 140, NUMBER 4A 15 NOVEMBER 1965

Self-Consistent Equations Including Exchange and Correlation Effects*

W. KOHN AND L. J. SHAM
University of California, San Diego, La Jolla, California
(Received 21 June 1965)

Note added in proof. We should like to point out that it is possible, formally, to replace the many-electron problem by an *exactly* equivalent set of self-consistent one-electron equations. This is accomplished quite simply by using the expression (2.2) [without the approximation (2.3)] in the energy variational principle. This leads to a set of equations, analogous to Eqs. (2.4)–(2.9), but with $\mu_{xc}(n)$ replaced by an effective one-particle potential v_{xc}, defined formally as

$$v_{xc}(\mathbf{r}) = \delta E_{xc}[n]/\delta n(\mathbf{r}).$$

Of course, an explicit form of v_{xc} can be obtained only if the functional $E_{xc}[n]$, which includes all many-body effects, is known. This effective potential will reproduce the exact density and the exact total energy is then given by

$$E = \sum_1^N \epsilon_i - \frac{1}{2}\int\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}\, d\mathbf{r}' + E_{xc}[n] - \int v_{xc}(\mathbf{r})\, n(\mathbf{r})\, d\mathbf{r}.$$

Of course, if we make the approximation (2.3) for E_{xc} the above exact formulation reverts to the approximate theory of Sec. II.

We first write

$$G[n] \equiv T_s[n] + E_{xc}[n], \tag{2.2}$$

where $T_s[n]$ is the kinetic energy of a system of noninteracting electrons with density[8] $n(\mathbf{r})$ and $E_{xc}[n]$ is, by our definition, the exchange and correlation energy of an interacting system with density $n(\mathbf{r})$. For an arbitrary $n(\mathbf{r})$, of course, one can give no simple exact expression for $E_{xc}[n]$. However, if $n(\mathbf{r})$ is sufficiently slowly varying, one can show[3] that

$$E_{xc}[n] = \int n(\mathbf{r})\epsilon_{xc}(n(\mathbf{r}))\, d\mathbf{r}, \tag{2.3}$$

FAQ and FHM:

#1: Since $F[n]$ is independent of the external potential, why not calculate F extremely accurately for one system and then use it for all others?

Misunderstood the meaning of "functional".

The most you can do for one system is calculate its energy and density very accurately and that will give you one point of the functional: The value of F for *that* density.

Then you could write down an expression for $F[n]$ that would reproduce your answer for that density, but there are infinitely many ways to do this.

Some expressions for $F[n]$ produce the exact answer for infinitely many systems.

Outline

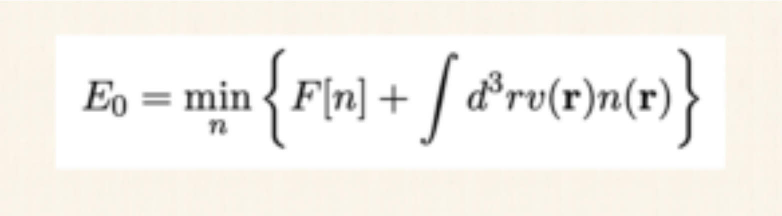
- **Simplest examples of density functionals**
- Chemical Potential
- Derivative Discontinuities
- Key errors (self-interaction, delocalization, static-correlation)

For only 1 electron, $\psi(\vec{r}) = \sqrt{n(\vec{r})}$

$$\int d^3r \sqrt{n(\vec{r})}\left(-\frac{1}{2}\nabla^2\sqrt{n(\vec{r})} + v(\vec{r})\sqrt{n(\vec{r})}\right) = \int_{d^3r} E \sqrt{n(\vec{r})}\sqrt{n(\vec{r})}$$

$$-\frac{1}{2}\int d^3r \sqrt{n(\vec{r})}\,\nabla^2\sqrt{n(\vec{r})} + \int d^3r\, v(\vec{r})\, n(\vec{r}) = E[n]$$

$$\underbrace{-\frac{1}{2}\int d\mathbf{r}\sqrt{n(\mathbf{r})}\nabla^2\sqrt{n(\mathbf{r})}}_{F[n] = \frac{1}{8}\int d\mathbf{r}\frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})}} + \int d\mathbf{r}\, v(\mathbf{r}) n(\mathbf{r}) = E[n]$$



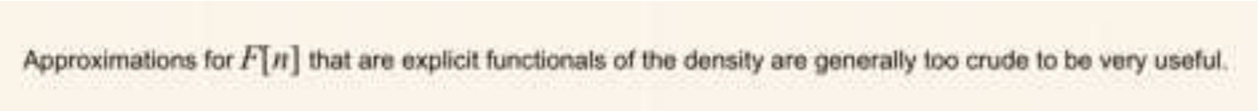
$$E_0 = \min_n \left\{ F[n] + \int d^3r\, v(\mathbf{r}) n(\mathbf{r}) \right\}$$

Reminders from yesterday:

$$F[n] = T_s[n] + \cancel{E_H[n] + E_{XC}[n]}$$

$E_H + E_{xc} = 0$ for 1 electron

Difficult and, in some ways still unresolved problem in DFT: approximate expressions for E_{xc} often do not cancel the Hartree for 1-electron systems.



Approximations for $F[n]$ that are explicit functionals of the density are generally too crude to be very useful.

"Orbital-free DFT"

$$\frac{\delta F[n]}{\delta n(\mathbf{r})} + v(\mathbf{r}) = \mu$$

Reference: *ABC of DFT*, by Kieron Burke
Ref.1 http://dft.uci.edu

Kinetic energy of M non-interacting and spinless fermions in 1d:

$$T_s[\{\phi_j\}] = \frac{1}{2}\int_{-\infty}^{+\infty} dx \sum_{j=1}^{M} \left|\frac{d\phi_j(x)}{dx}\right|^2$$

Is there some way to get T_s *without* evaluating all the orbitals?

Yes: Write it as a density functional, i.e., an integral over some function of $n(x)$,

$$n(x) = \sum_{j=1}^{M} |\phi_j(x)|^2$$

Simplest choice: a local approximation:

$$T_s^{\mathrm{loc}}[n] = \frac{\pi^2}{6}\int_{-\infty}^{+\infty} dx\ n^3(x)$$

Construction motivated by:

$$\varepsilon_j = \frac{\pi^2 j^2}{2L^2} \qquad j = 1,2,3,\ldots$$

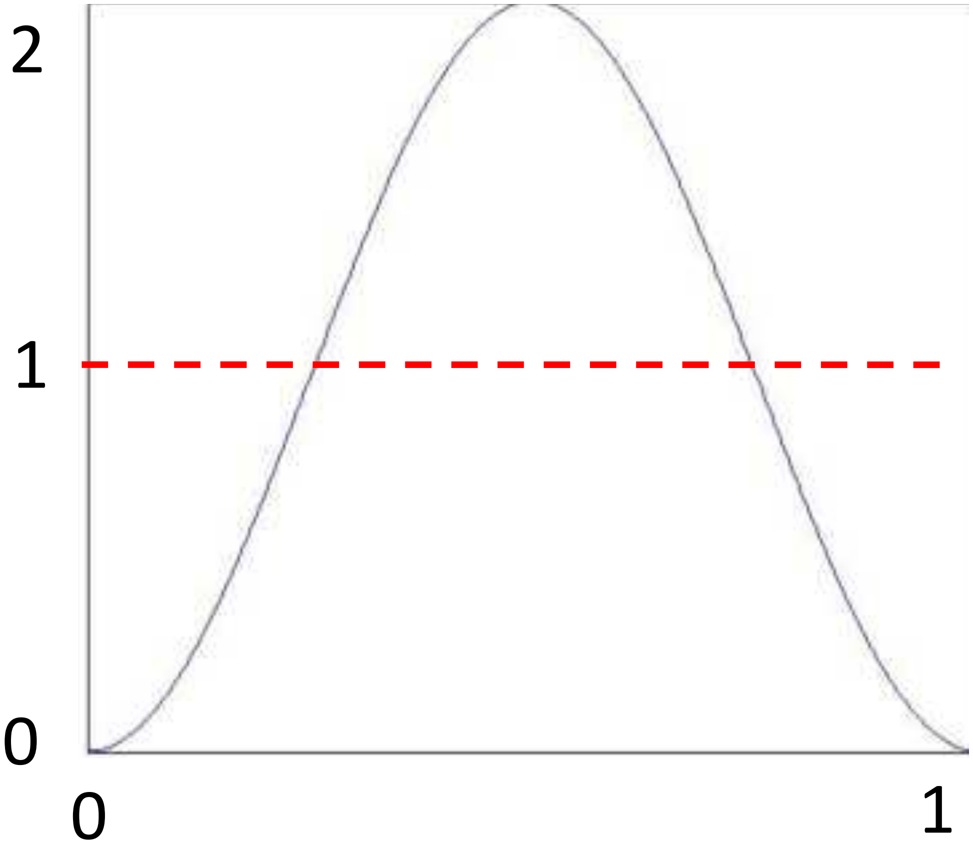
$$E = \frac{\pi^2}{2L^2}\sum_{j=1}^{M} j^2 = \frac{\pi^2}{2L^2} M(M+1)(2M+1)/6$$

As M increases, density inside the box tends to constant $n = M / L$, so:

$$E \rightarrow \frac{\pi^2}{6} n^3 L$$

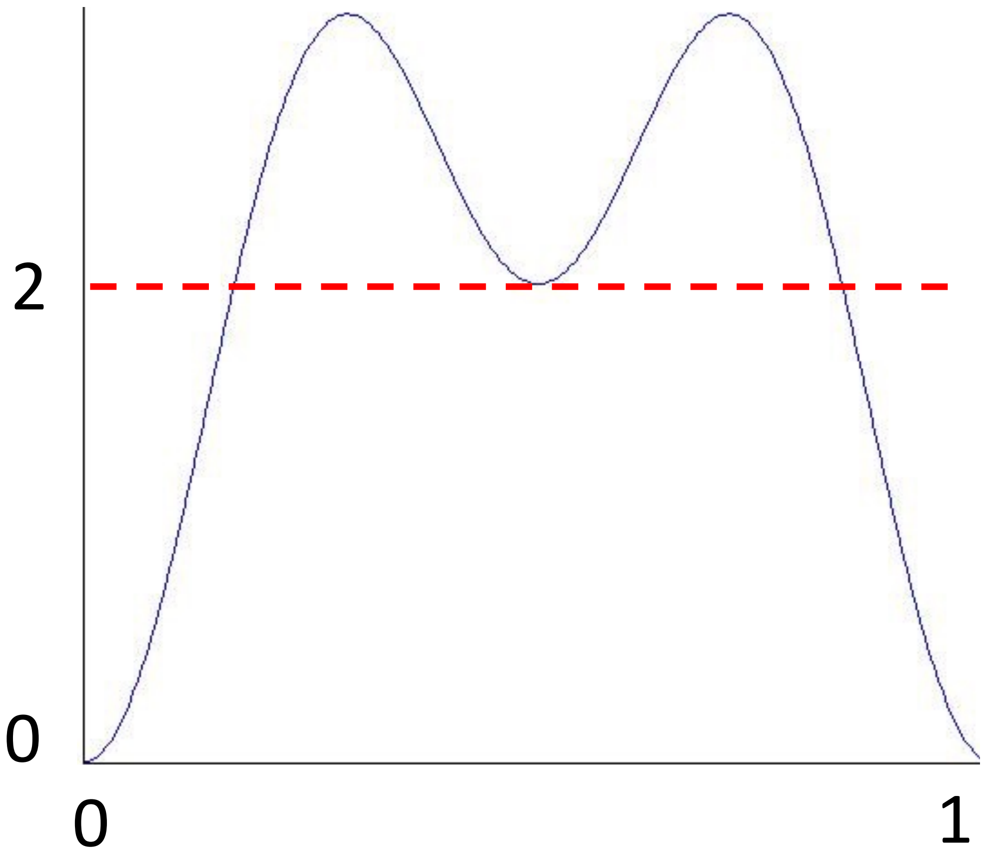
$$\frac{\pi^2}{6}\int dx\, n^3(x)$$

Particles in 1d-box



M	T_s^{loc}	T_s	%err
1	4.112	4.934	-17
2	21.79	24.67	-12
3	62.92	69.09	-9
25	26875	27264	-1

Particles in 1d-box



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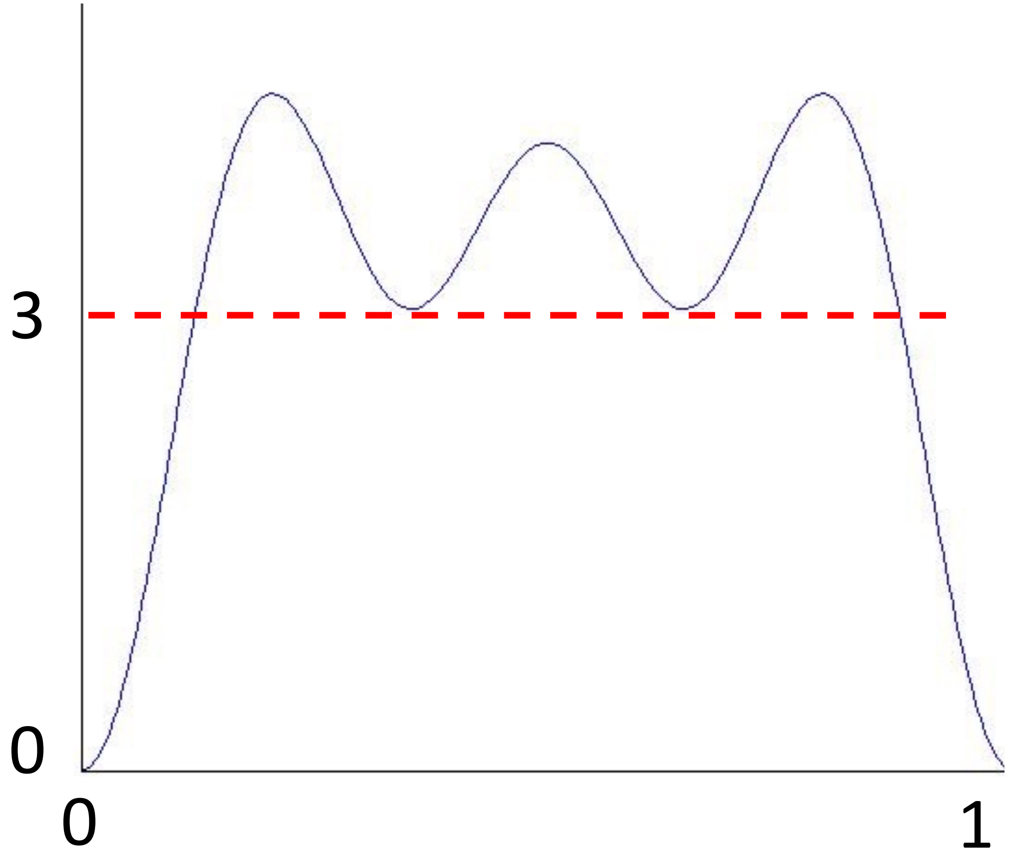

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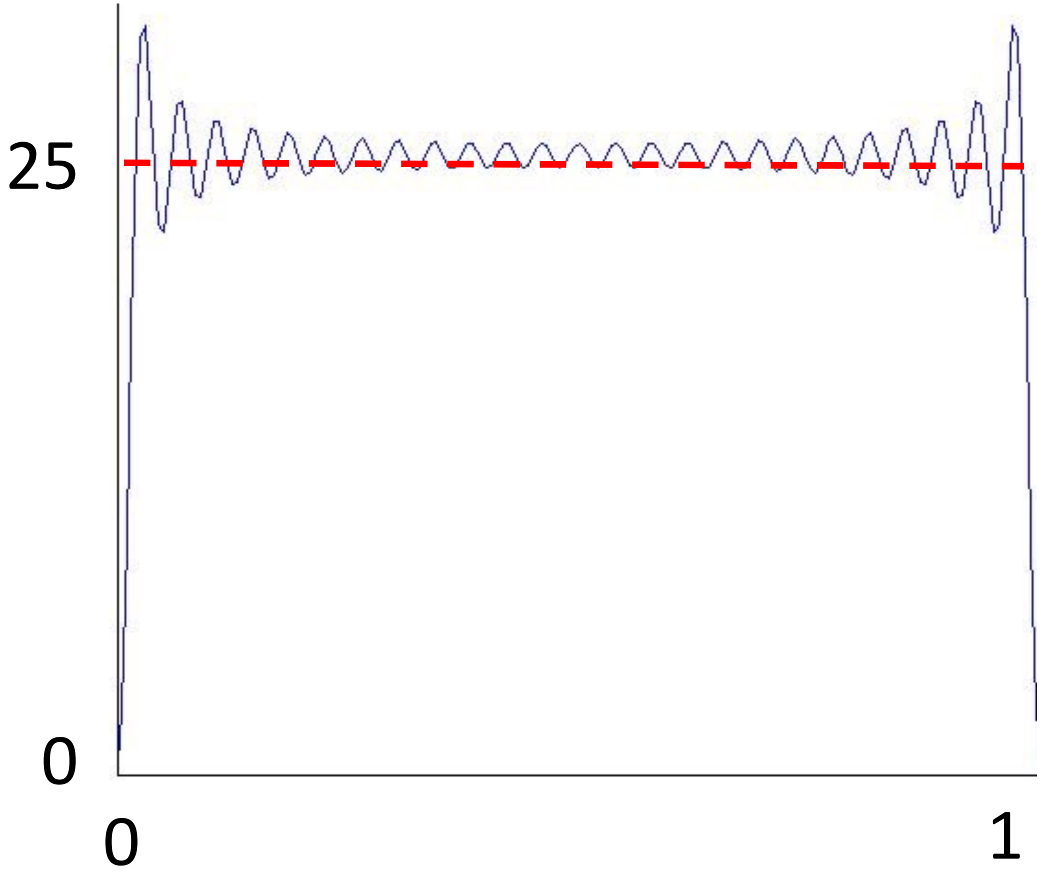

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In KS-DFT, T_s is not calculated this way, but it is obtained "exactly" from the orbitals.

- $T_s^{\text{loc}}[n]$: simplest example of functional design by satisfaction of exact constraint.

- Local approximations work best for large M, worst for small M.

- Local approximations are crudely correct, but miss details.

- OK, I have a functional. What do I do with it?

$$\frac{\delta F[n]}{\delta n(\mathbf{r})} + v(\mathbf{r}) = \mu$$

For our non-interacting 1d-spinless fermions:

$$\frac{\delta T_S}{\delta n(x)} + v(x) = \mu \qquad T_S[n] = \frac{\pi^2}{6} \int dx\, n^3(x)$$

$$\frac{\pi^2}{6}\, 3\, n^2(x) + v(x) = \mu$$

$$\frac{\pi^2}{2} n^2(x) = \mu \quad \text{inside the box}$$

$$n(x) = \begin{cases} \frac{1}{\pi}\sqrt{2\mu} & \text{, inside the box.} \\ 0 & \text{, outside.} \end{cases}$$

So: $$\frac{1}{\pi}\int_0^L dx\sqrt{2\mu} = M$$

and: $$\mu = \frac{M^2\pi^2}{2L^2} = -(E(M-1) - E(M))$$

FAQ and FHM:

#1: Since $F[n]$ is independent of the external potential, why not calculate F extremely accurately for one system and then use it for all others?

Misunderstood the meaning of "universal functional".

#2: What is the physical meaning of the Lagrange multiplier μ?

$$\frac{\delta F[n]}{\delta n(\mathbf{r})} + v(\mathbf{r}) = \underset{\downarrow}{\boxed{\mu}}$$

"Chemical potential"

$$\mu = \left.\frac{\partial E}{\partial N}\right|_{v}$$

M electrons

$$\int d^3r\, \delta n(\vec{r}) = 0$$

$$\int d^3r\, \underbrace{\frac{\delta F[n]}{\delta n(\vec{r})}}_{+C}\, \delta n(\vec{r})$$

Derivative of the energy with respect to an average number of electrons; e.g. system in contact with a reservoir of electrons.

PHYSICAL REVIEW VOLUME 136, NUMBER 3B 9 NOVEMBER 1964

Inhomogeneous Electron Gas*

P. Hohenberg†
École Normale Superieure, Paris, France

AND

W. Kohn‡
École Normale Superieure, Paris, France and Faculté des Sciences, Orsay, France
and
University of California at San Diego, La Jolla, California

(Received 18 June 1964)

$$\frac{\delta}{\delta n}\left\{E_v[n]-\mu\int n(\mathbf{r})d\mathbf{r}\right\}=0. \qquad (67)$$

$$\int d\mathbf{r}\delta n(\mathbf{r}) = 0$$

$$\delta F = \int d\mathbf{r} \left(\frac{\delta F[n]}{\delta n(\mathbf{r})} \right) \delta n(\mathbf{r})$$

So, $\frac{\delta F[n]}{\delta n(\mathbf{r})}$ is only defined to within an arbitrary additive constant.

$$\int d\mathbf{r} n(\mathbf{r}) = M$$

e.g., for only 1 electron,

$$F[n] = \frac{1}{8} \int d\mathbf{r} \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})}$$

$$\frac{\delta F[n]}{\delta n(\mathbf{r})} = \frac{1}{8} \left(\frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})^2} - 2 \frac{\nabla^2 n(\mathbf{r})}{n(\mathbf{r})} \right)$$

Schrödinger's equation $\frac{\delta F[n]}{\delta n(\mathbf{r})} + v(\mathbf{r}) = \mu = E\,(1) = -\ I\,(1)$

$$\mu \sim \left(\frac{\partial E}{\partial N}\right)_{v(\mathbf{r})}$$

$$\frac{\partial E}{\partial N} = \lim_{\Delta N \to 0} \frac{E(N+\Delta N) - E(N)}{\Delta N}$$

What can this mean?
(Check Ref.8)

Why generalize DFT to non-integer numbers of electrons?:

(1) DFT is based on a variational principle, so it is convenient to not have to worry about density variations that do not conserve the number of particles.

(2) Many physical situations where it is convenient to treat N as a continuous variable.

Chapter 7 in "Quantum Theory of the Electron Liquid", G.F. Giuliani and G. Vignale (Cambridge University Press, 2005). Ref.6

$$\hat{K} = \hat{H} - \mu\hat{N}$$

$$\mu \longleftrightarrow N$$

$$v(\mathbf{r}) \longleftrightarrow n(\mathbf{r})$$

Molecule with M electrons

Metal with work function $-\mu$

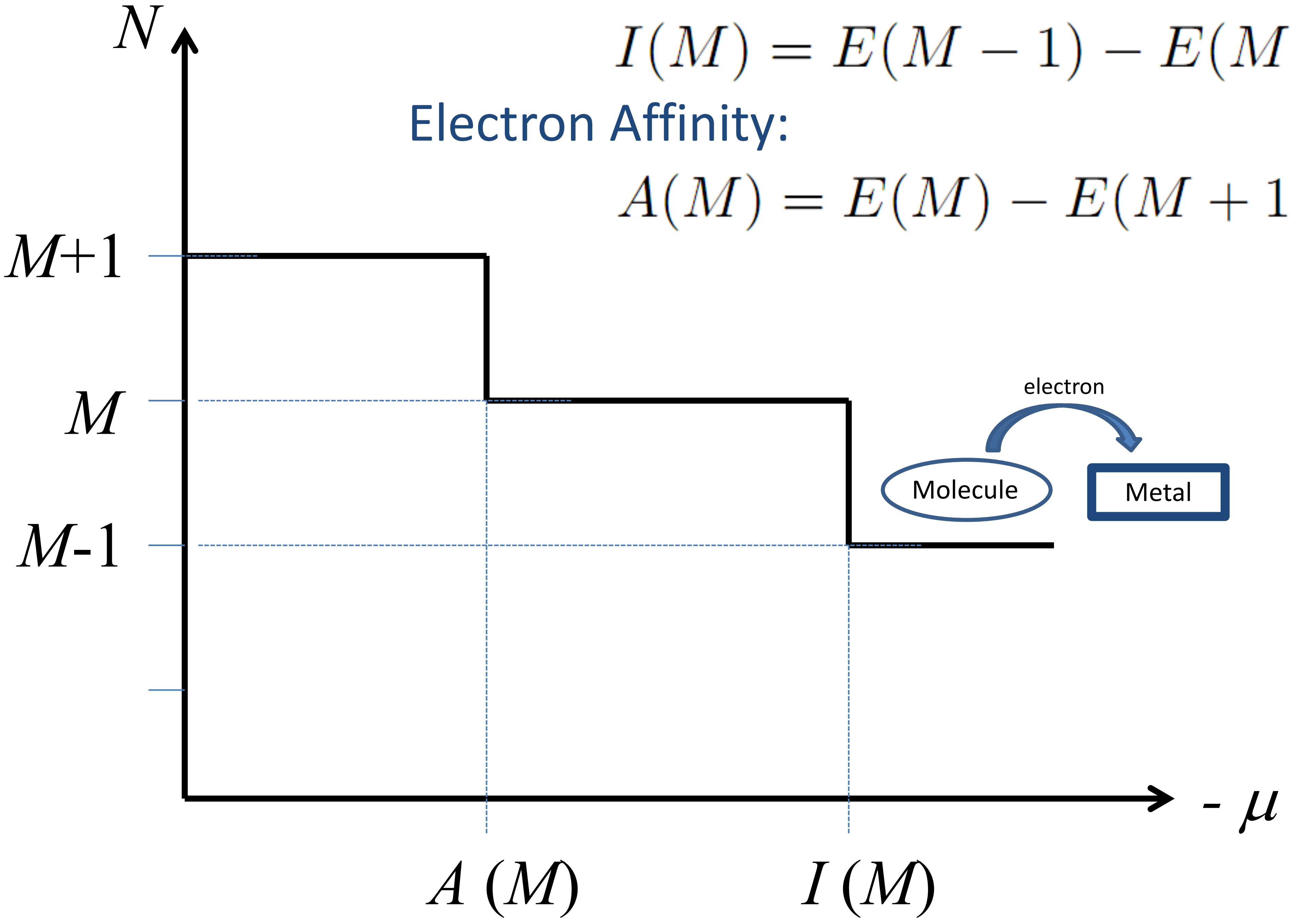
J.P. Perdew, in NATO ASI Ser., Ser.B 123 (Density Funct. Methods Phys.), 265 (1985). Ref.5

Ionization Potential:

$$I(M) = E(M-1) - E(M)$$

Electron Affinity:

$$A(M) = E(M) - E(M+1)$$



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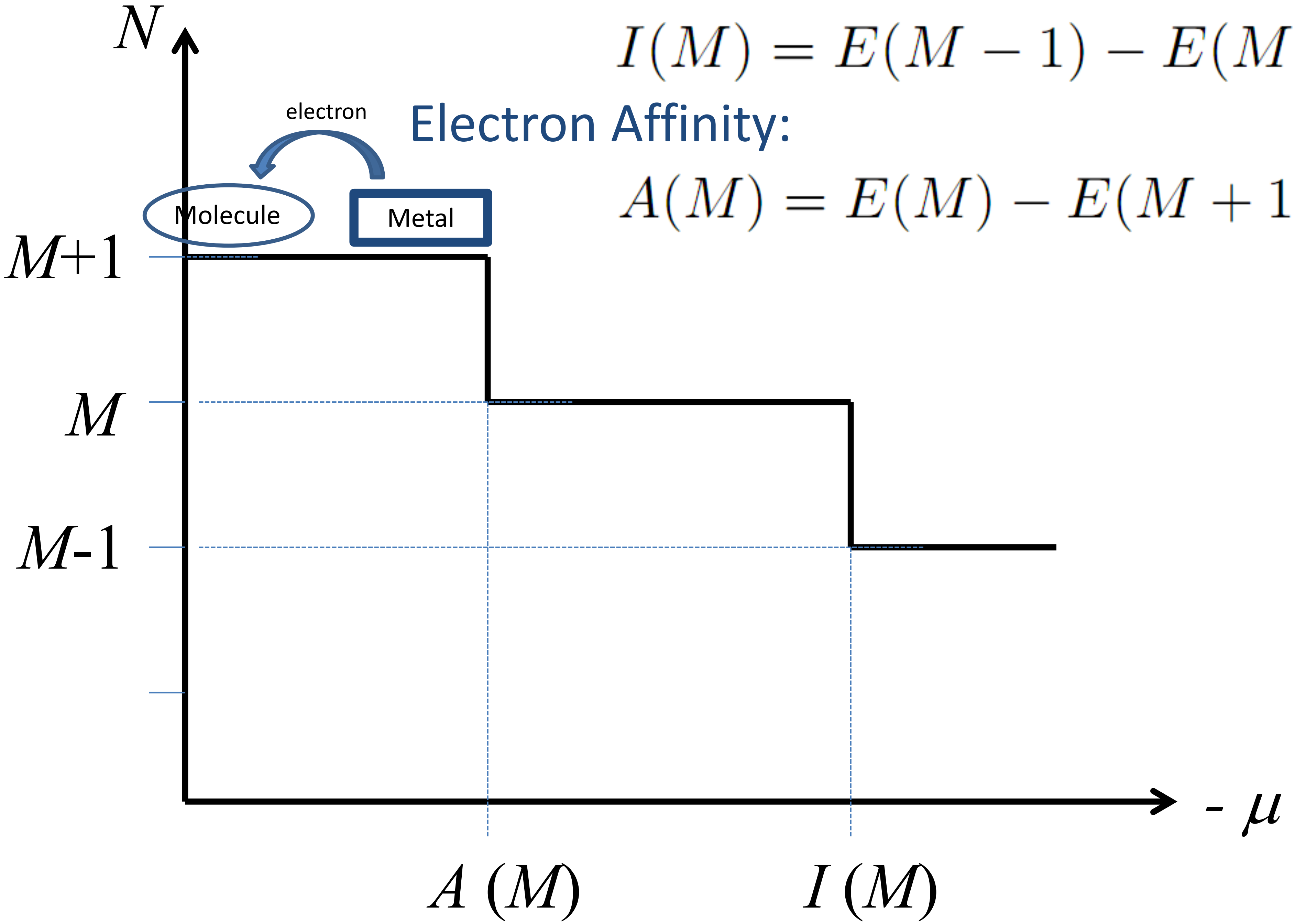
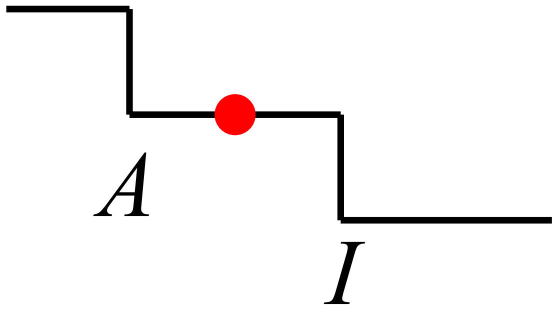
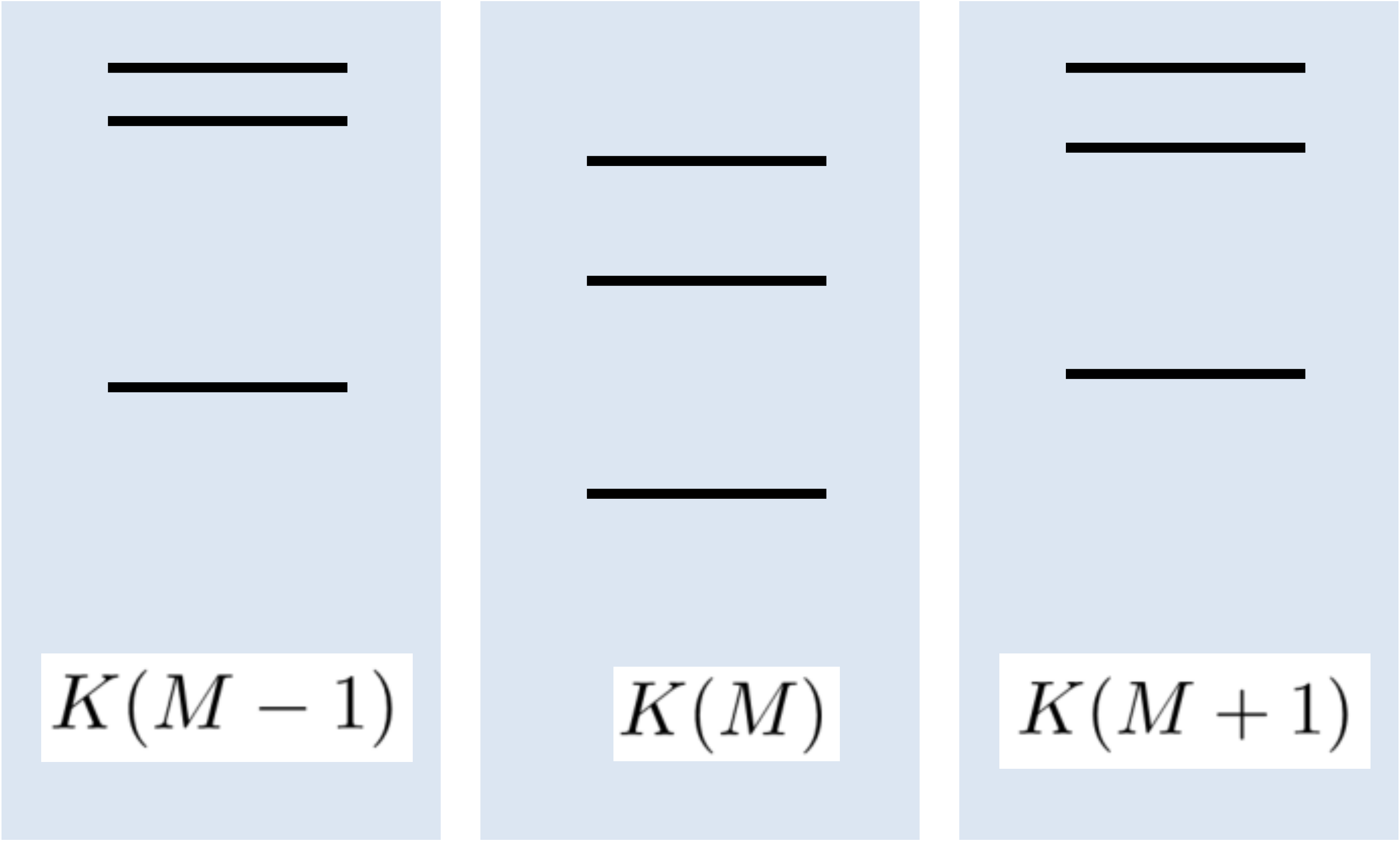
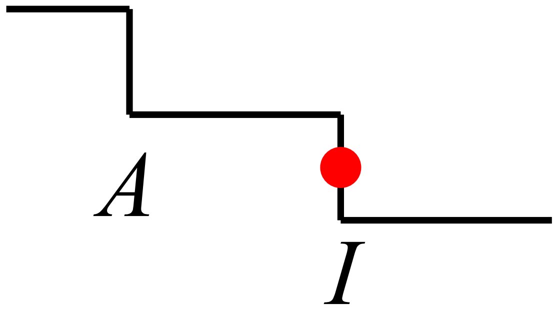


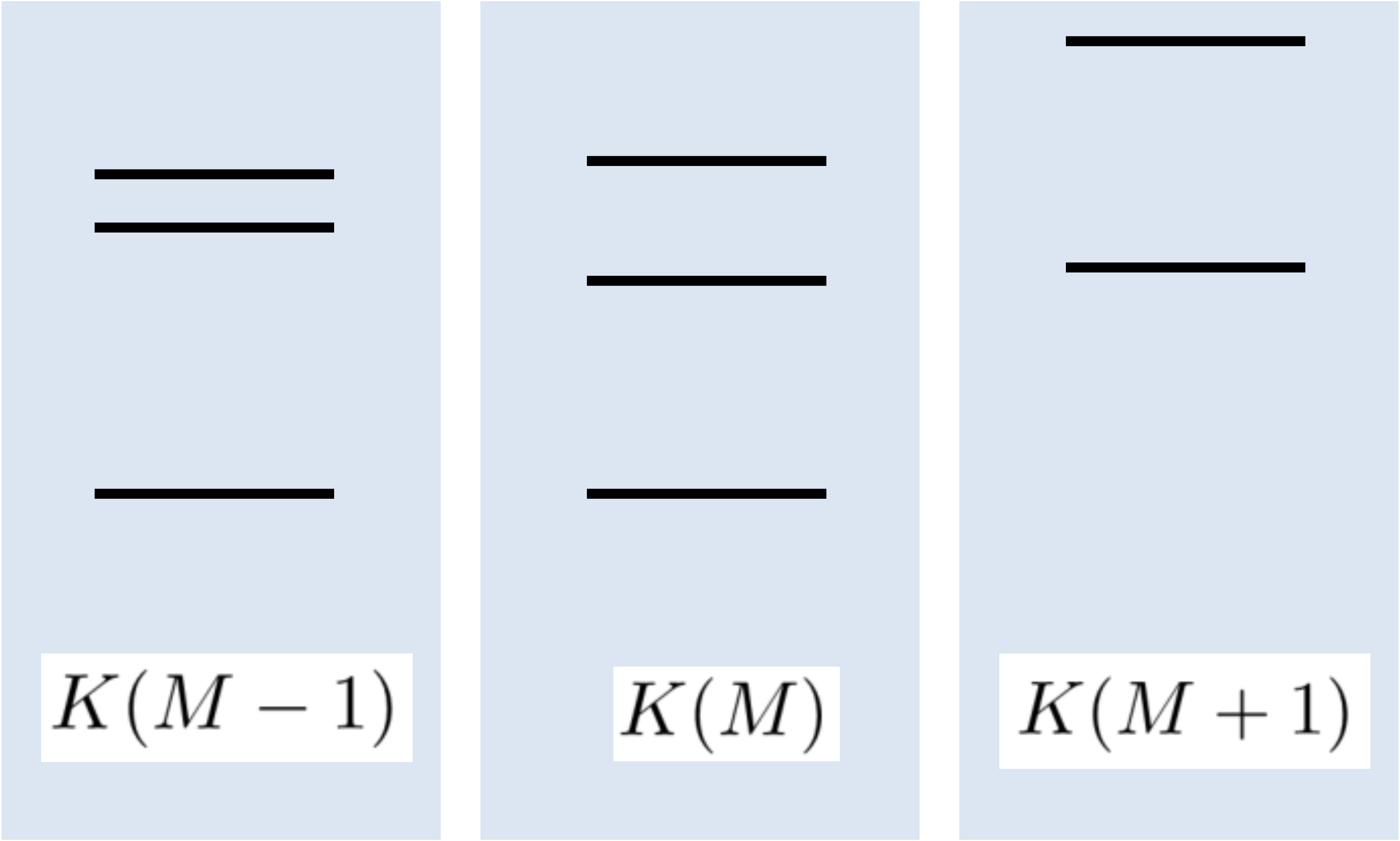


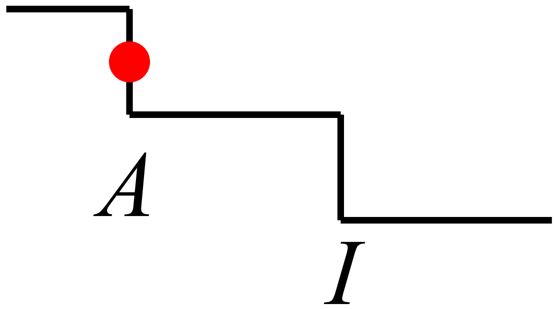
$$A(M) < -\mu < I(M)$$



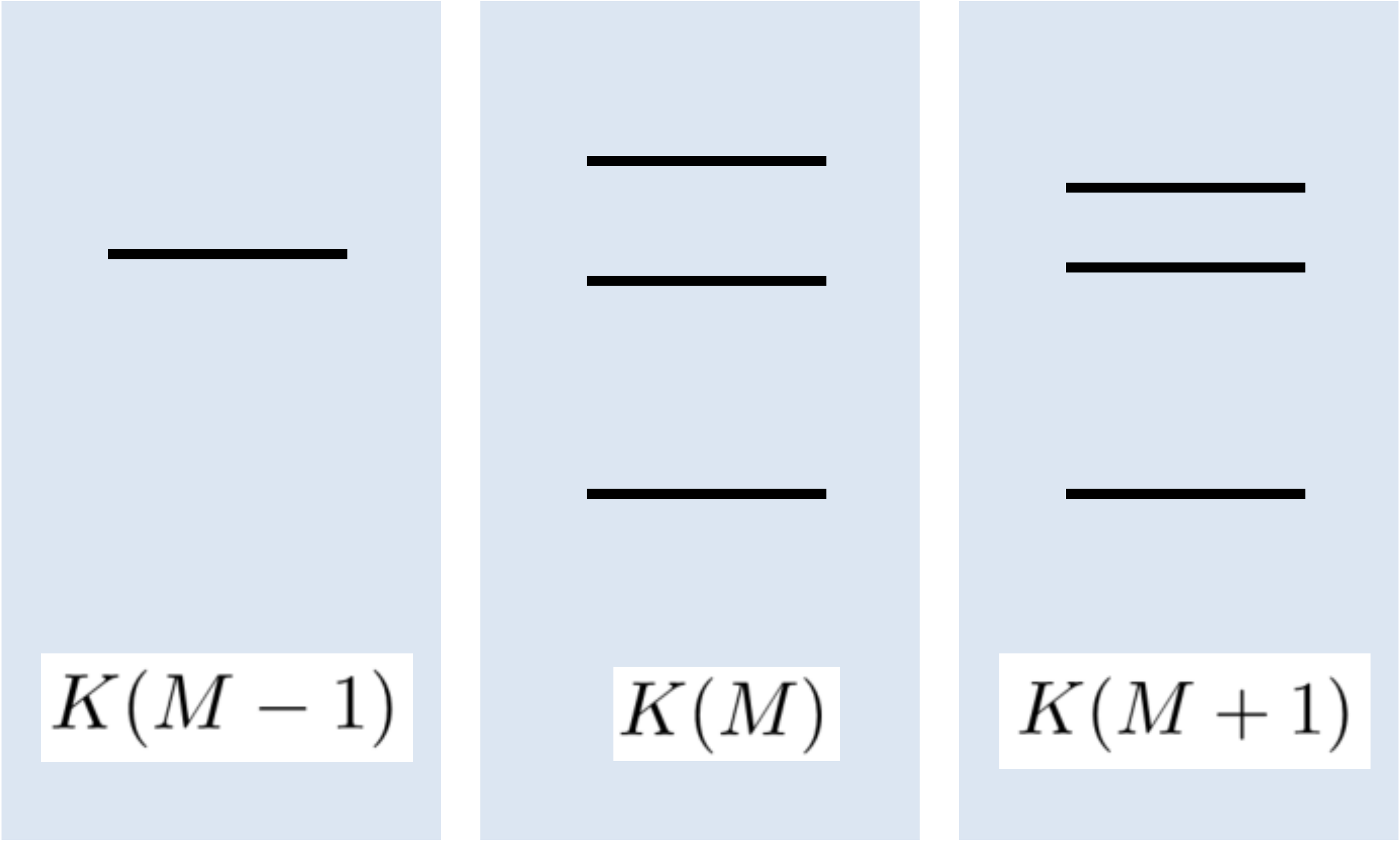


$$-\mu = I(M)$$





$$A(M) < -\mu < I(M)$$



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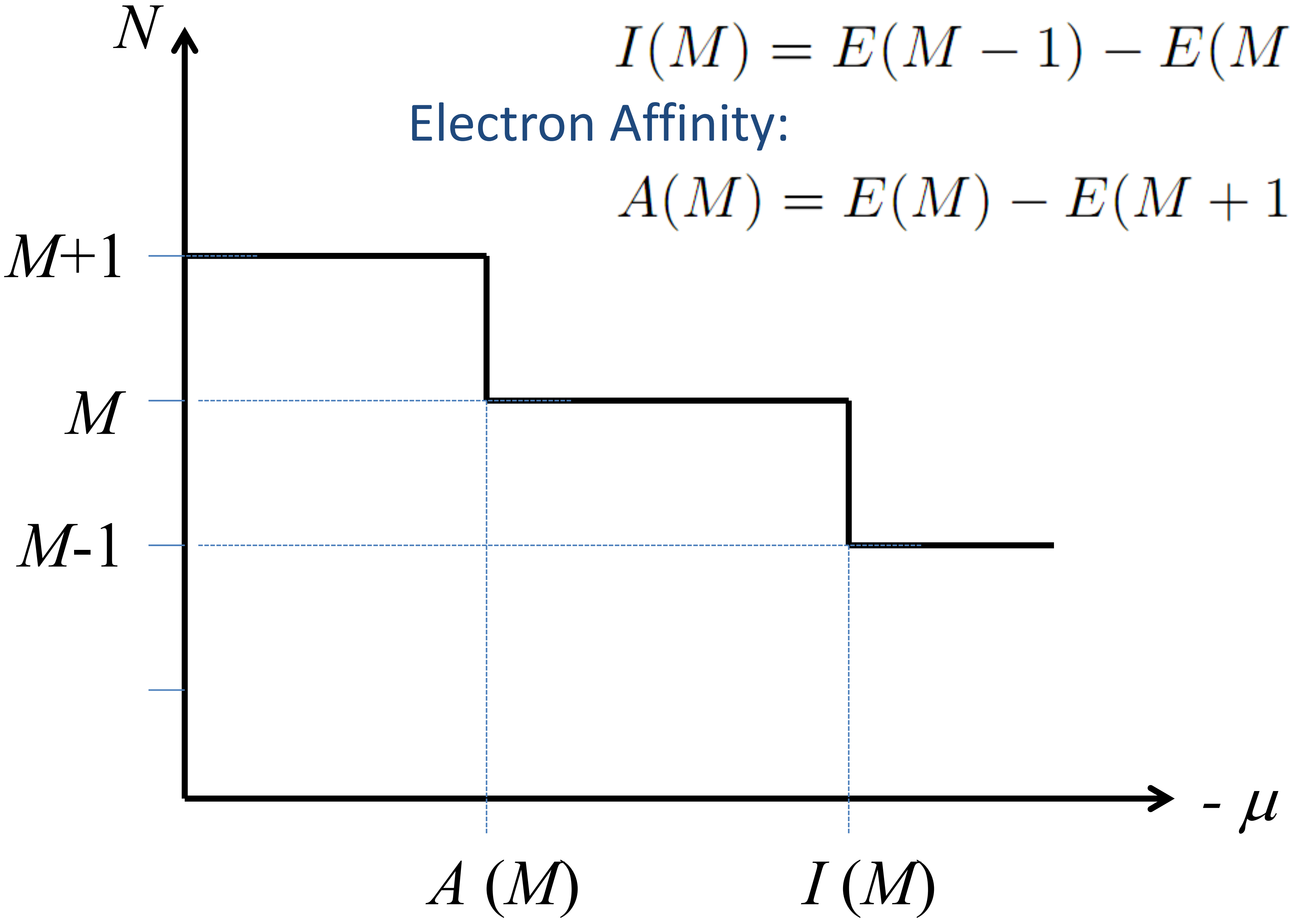

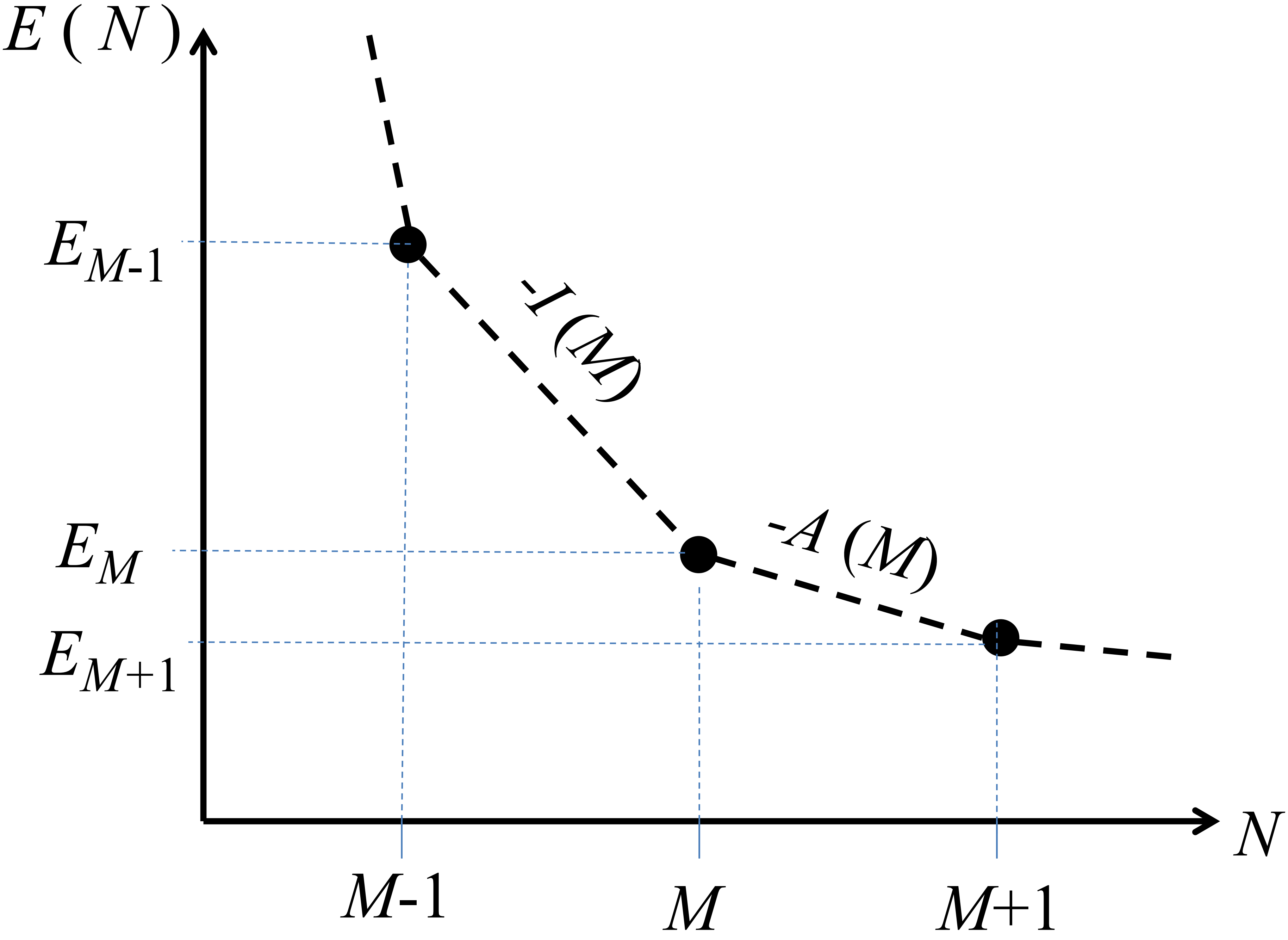

$E(N)$
$E_{M\text{-}1}$
E_M
E_{M+1}
$-I(M)$
$-A(M)$
N
M-1
M
M+1

FAQ and FHM:

#1: Since $F[n]$ is independent of the external potential, why not calculate F extremely accurately for one system and then use it for all others?

Misunderstood the meaning of "universal functional".

#2: **What is the physical meaning of the Lagrange multiplier μ ?**

That depends. Could be –I or could be –A.

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#3: I'm doing a band-structure calculation with a good semi-local functional. Why is my band-gap "wrong"?

Outline

- Simplest possible examples of density functionals
- Chemical Potential
- **Derivative Discontinuities**
- Key errors (self-interaction, delocalization, static-correlation)

$$\Omega[n] = \tilde{F}[n] + \int d\mathbf{r}\, [v(\mathbf{r}) - \mu]\, n(\mathbf{r})$$

$$\tilde{F}[n] \equiv \min_{\hat{\Gamma} \to \; n(\mathbf{r})} Tr\left[\hat{\Gamma}\left(\hat{T} + \hat{V}_{ee}\right)\right]$$

$$\frac{\delta \tilde{F}[n]}{\delta n(\mathbf{r})} = \mu - v(\mathbf{r})$$

J.P. Perdew, R.G. Parr, M. Levy, J.L. Balduz, Phys. Rev. Lett. **49**, 1691 (1982).

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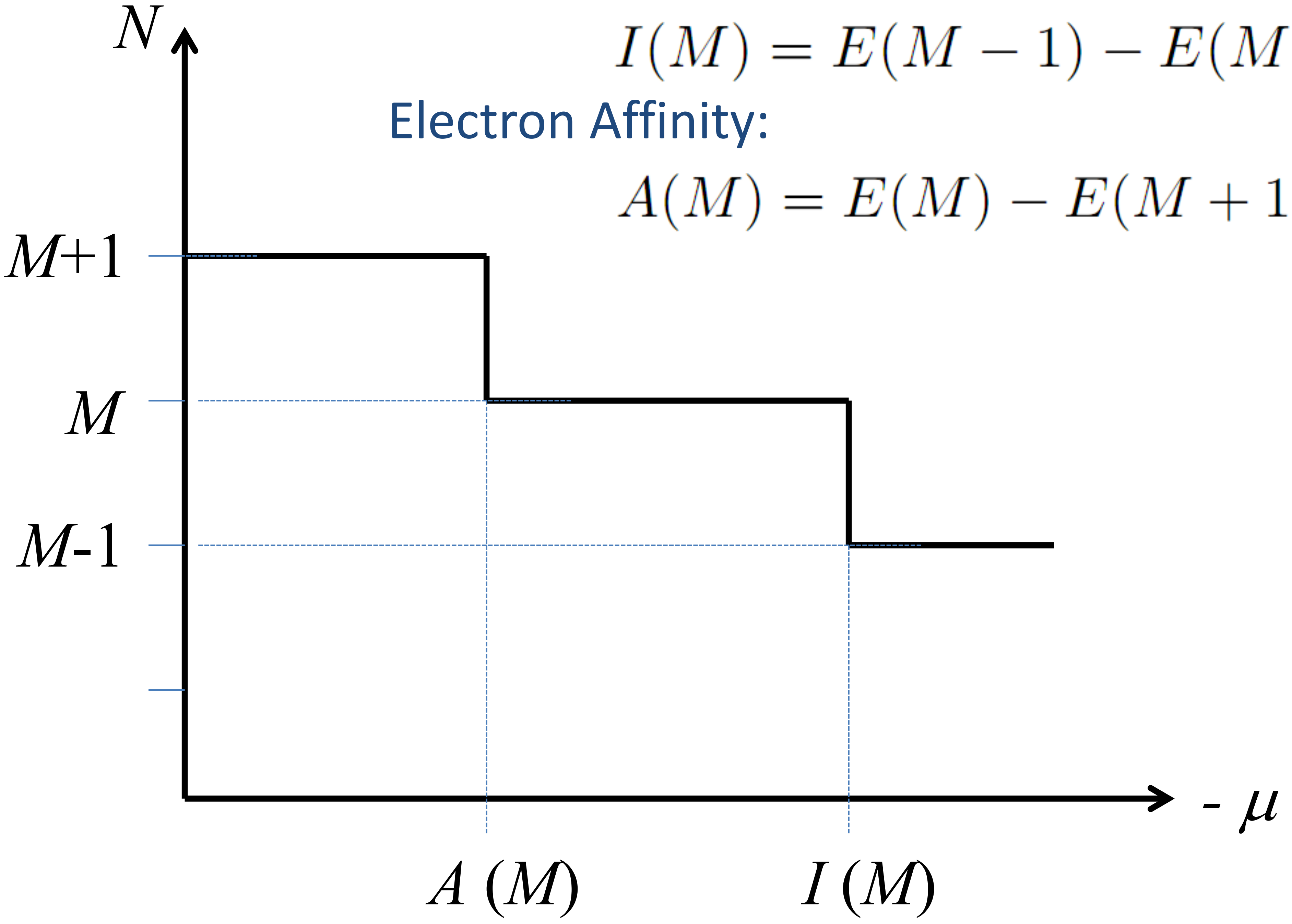

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$$\tilde{F}[n] \equiv \min_{\hat{\Gamma}\to\ n(\mathbf{r})} Tr\left[\hat{\Gamma}\left(\hat{T} + \hat{V}_{ee}\right)\right]$$

$$\frac{\delta \tilde{F}[n]}{\delta n(\mathbf{r})} = \mu - v(\mathbf{r})$$

A bit above M: $$\left.\frac{\delta \tilde{F}[n]}{\delta n(\mathbf{r})}\right|_{n_M^+(\mathbf{r})} = -A(M) - v(\mathbf{r})$$

A bit below M: $$\left.\frac{\delta \tilde{F}[n]}{\delta n(\mathbf{r})}\right|_{n_M^-(\mathbf{r})} = -I(M) - v(\mathbf{r})$$

Fundamental gap:

$$\left.\frac{\delta\tilde{F}[n]}{\delta n(\mathbf{r})}\right|_{n_M^+(\mathbf{r})} - \left.\frac{\delta\tilde{F}[n]}{\delta n(\mathbf{r})}\right|_{n_M^-(\mathbf{r})} \underset{\text{Koopmans'}}{=} \overset{-\varepsilon_{\text{HOMO}}}{I(M)} - A(M) \equiv E_g$$

Kohn-Sham gap:

$$\left.\frac{\delta\tilde{T}_s[n]}{\delta n(\mathbf{r})}\right|_{n_M^+(\mathbf{r})} - \left.\frac{\delta\tilde{T}_s[n]}{\delta n(\mathbf{r})}\right|_{n_M^-(\mathbf{r})} = \overset{-\varepsilon_{\text{HOMO}}}{I_s(M)} - \overset{-\varepsilon_{\text{LUMO}}}{A_s(M)} \equiv E_{g,KS}$$

$$\tilde{E}_{\text{XC}}[n] = \tilde{F}[n] - \tilde{T}_s[n] - E_{\text{H}}[n]$$

$$\Delta_{\text{XC}} \equiv \left.\frac{\delta\tilde{E}_{\text{XC}}[n]}{\delta n(\mathbf{r})}\right|_{n_M^+(\mathbf{r})} - \left.\frac{\delta\tilde{E}_{\text{XC}}[n]}{\delta n(\mathbf{r})}\right|_{n_M^-(\mathbf{r})} = E_g - E_{g,KS}$$

Band gaps (eV) of selected semiconductors and insulators

(table 7.1 from Ref. 6)

	Diamond	Si	Ge	LiCl	GaAs
LDA	3.9	0.52	0.07	6.0	0.12
Expt.	5.48	1.17	0.744	9.4	1.52

$$\Delta_{\rm XC} \equiv \left.\frac{\delta \tilde{E}_{\rm XC}[n]}{\delta n(\mathbf{r})}\right|_{n_M^+(\mathbf{r})} - \left.\frac{\delta \tilde{E}_{\rm XC}[n]}{\delta n(\mathbf{r})}\right|_{n_M^-(\mathbf{r})} = E_g - E_{g,KS}$$

#3: I’m doing a band-structure calculation with a good semi-local functional. Why is my band-gap “wrong”?

Lack of derivative discontinuity in approximate functional.

FAQ and FHM:

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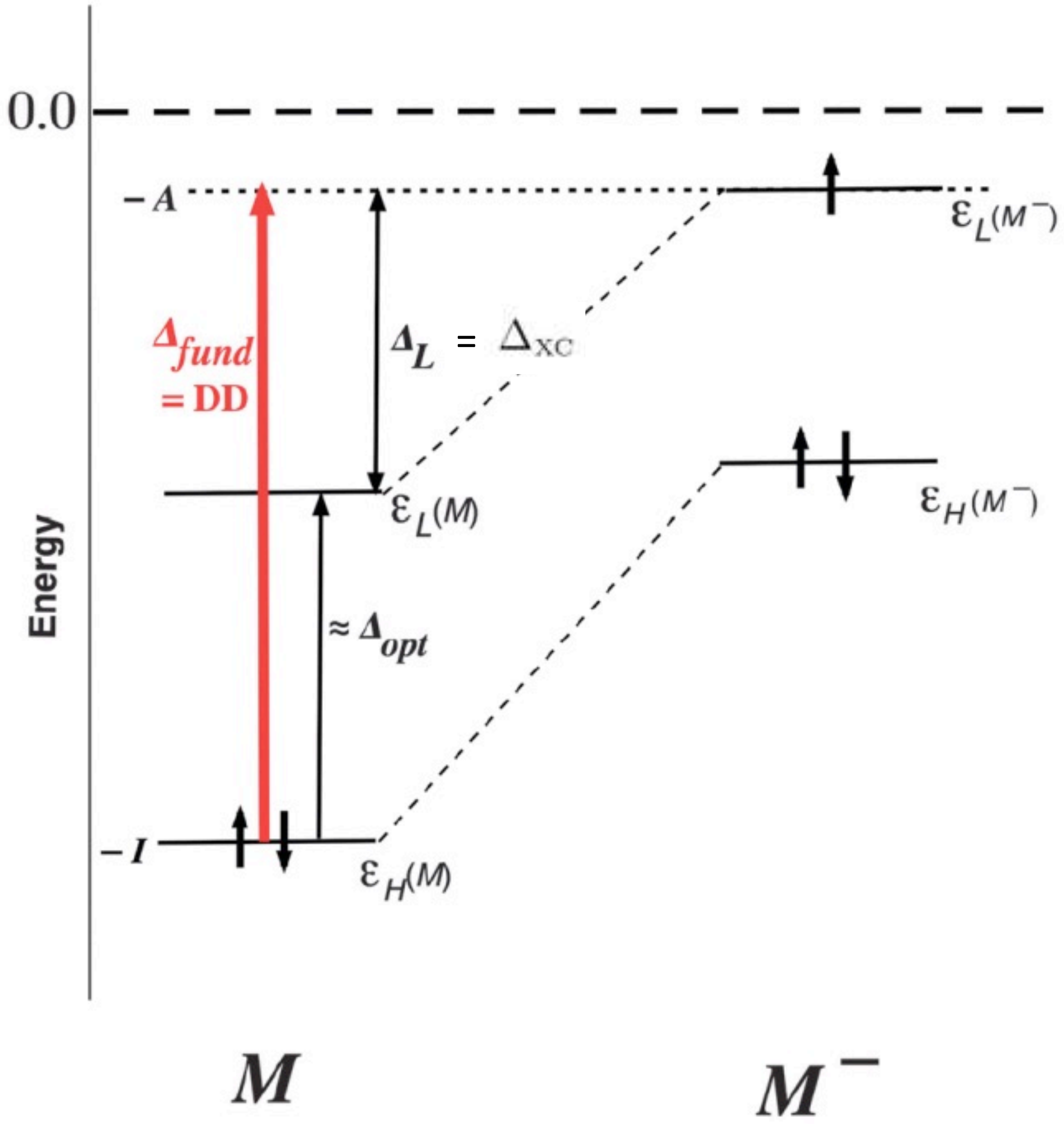

Ref.7

From: E.J. Baerends, O.V. Gritsenko, and R. van Meer, Phys. Chem. Chem. Phys. **15**, 16408 (2013).

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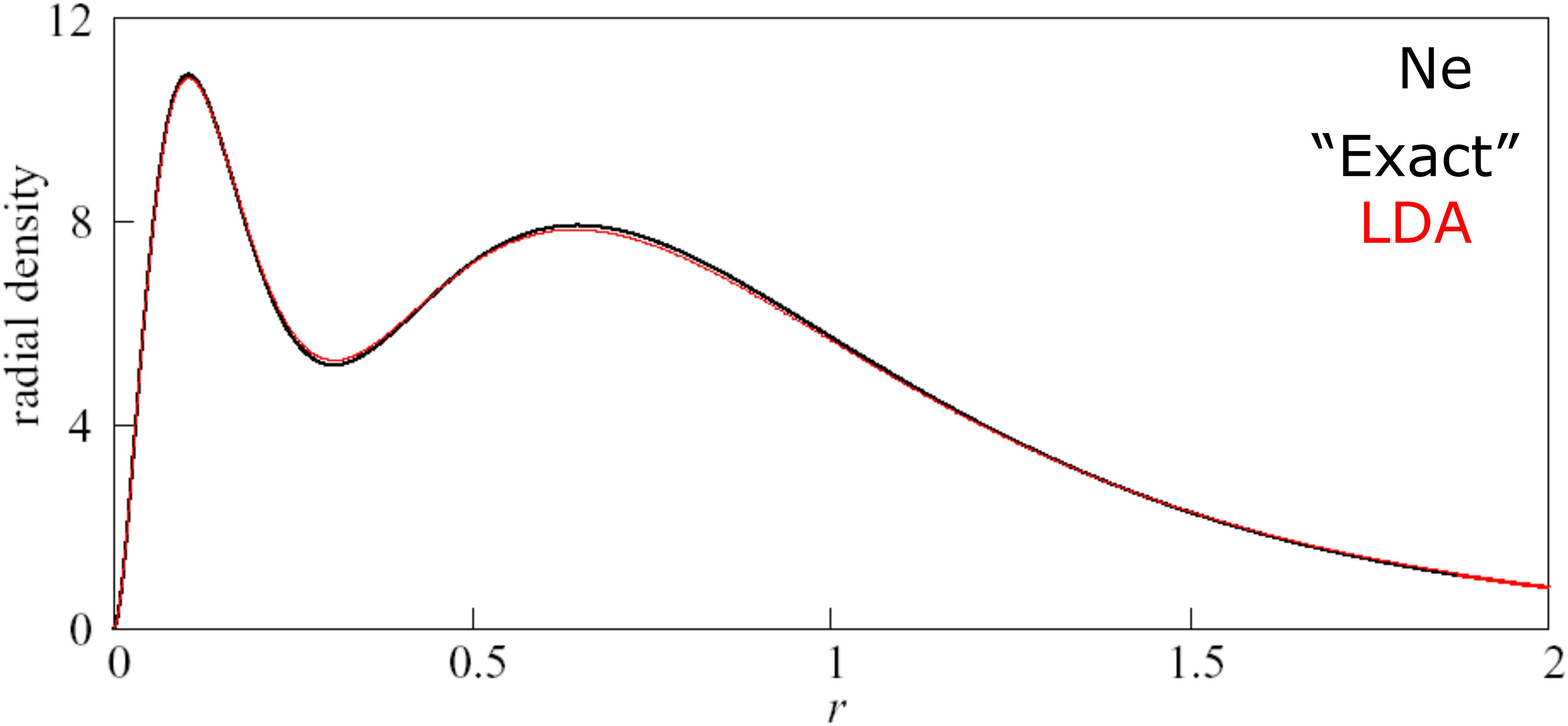
#4: Do "good densities" imply "good energies" ?

Not necessarily.



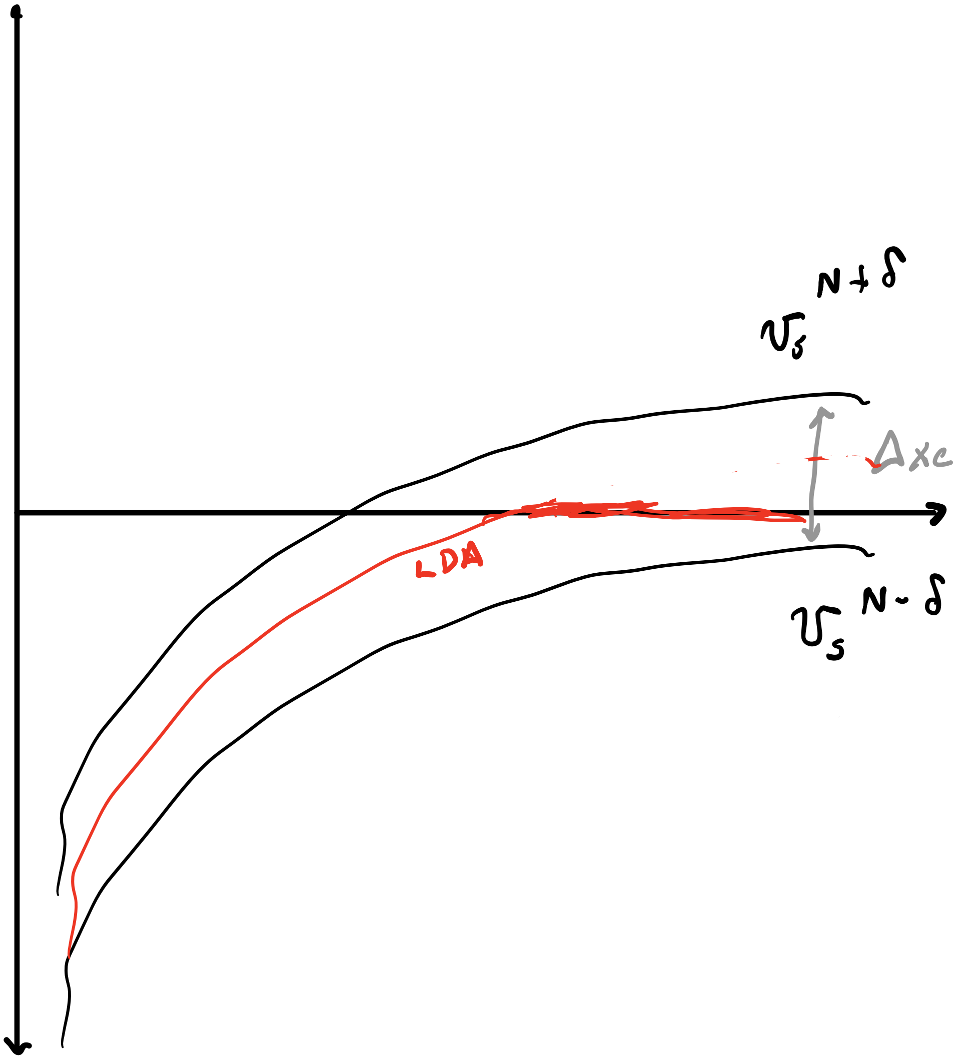
$$\varepsilon_{\text{HOMO}} = -\,I \;= -\,0.793\text{ H} = E(\text{Ne}) - E(\text{Ne}^{+})$$

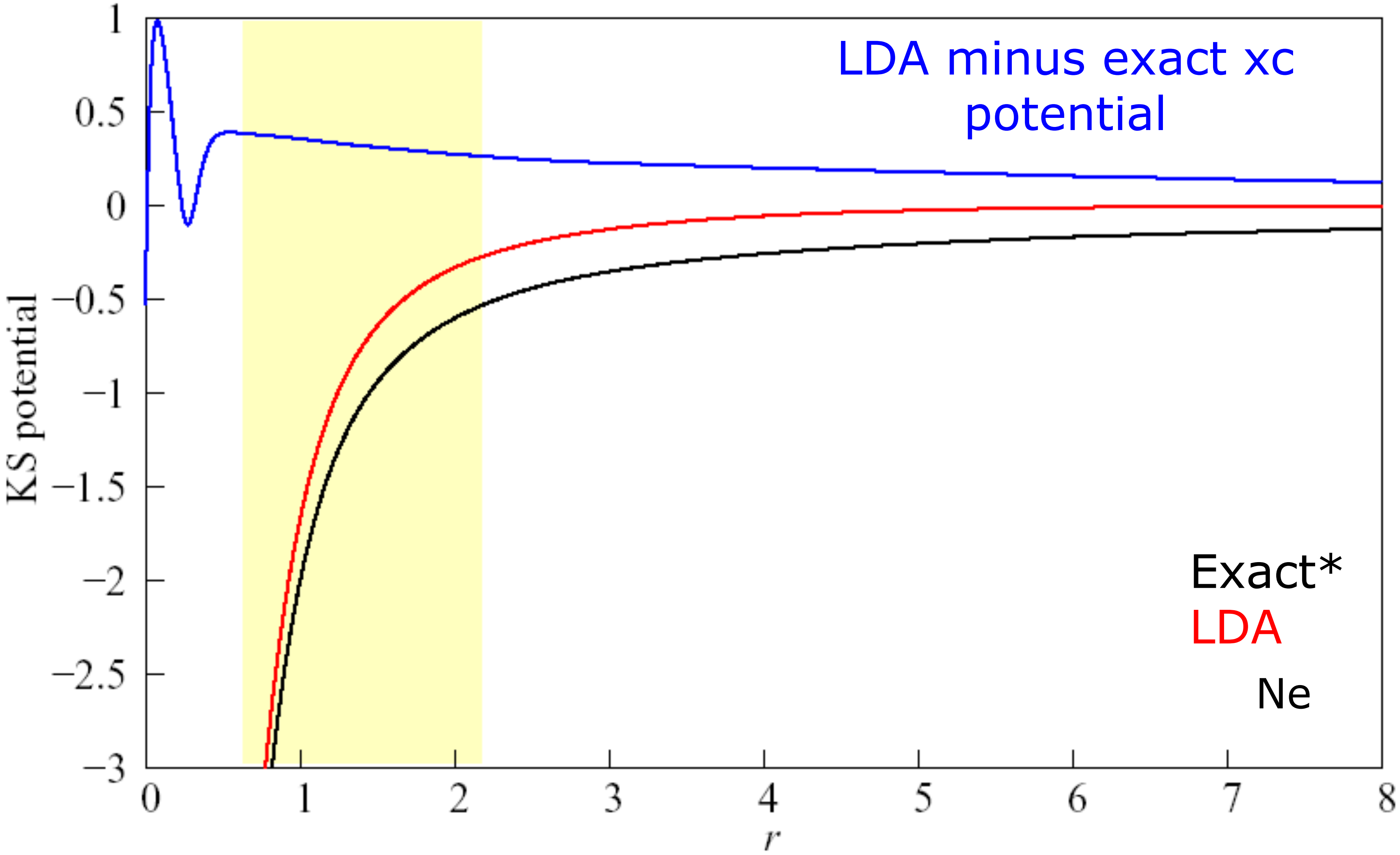
$$\varepsilon_{\text{HOMO}} = -\,0.793\text{ H}$$

$$\varepsilon_{\text{HOMO}} = -\,0.498\text{ H}$$

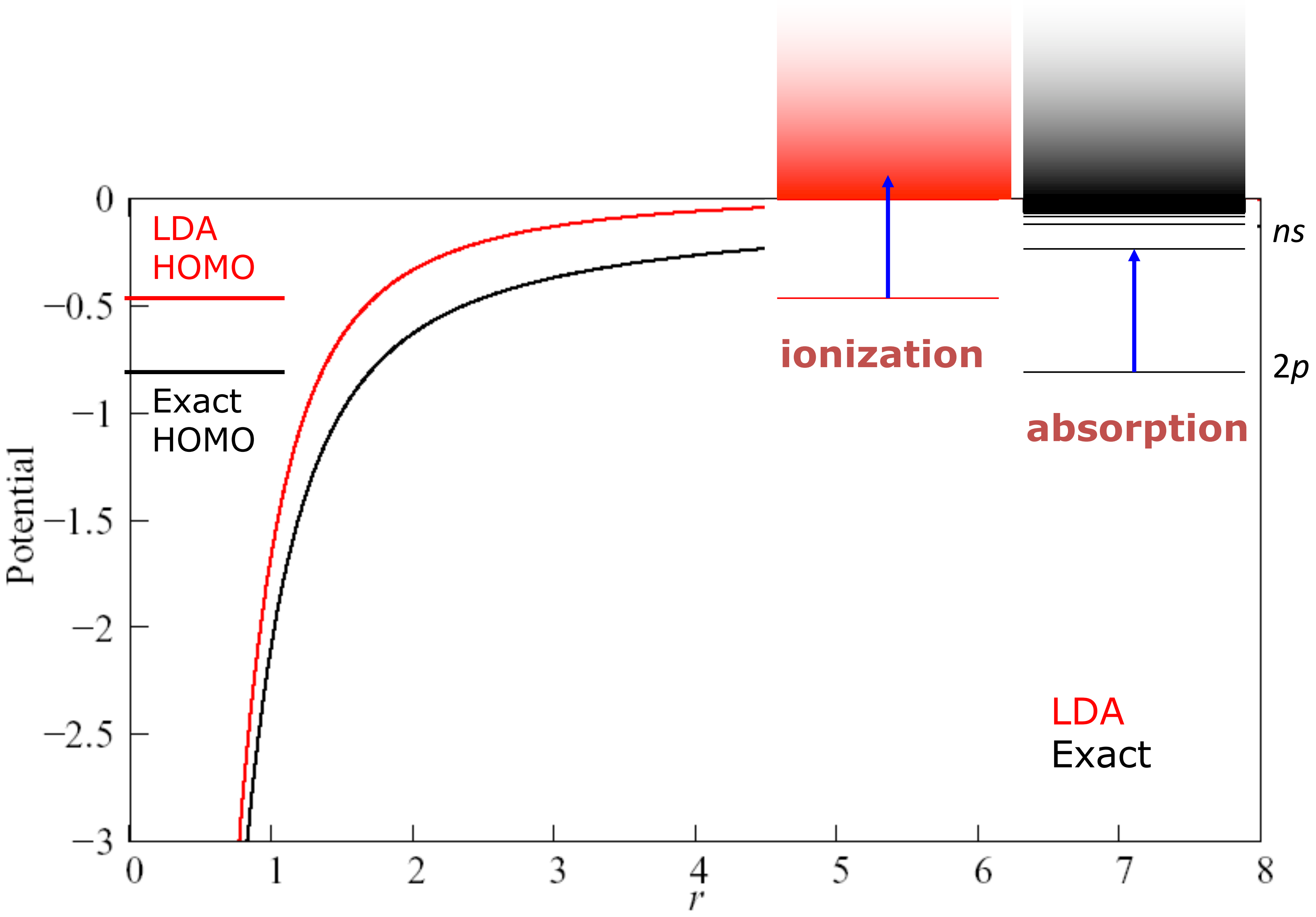
$$E(\text{Ne}^{+}) - E(\text{Ne}) = -127.400 + 128.233 \;= 0.833\text{ H}$$

Y. Shi, V. Chávez, and AW, "*n2v: A density-to-potential inversion suite*", WIREs Comput Mol. Sci. **12**, e1617 (2022).


$v_s^{N+\delta}$
Δ_{xc}
LDA
$v_s^{N-\delta}$



* C.J. Umrigar and X. Gonze, in *Proceedings of the Mardi Gras ’93 Conference*, ed. D.A. Browne *et al* .,(World Scientific, 1993).


LDA
HOMO
Exact
HOMO
ionization
absorption
ns
2p
LDA
Exact
Potential
r
0
−0.5
−1
−1.5
−2
−2.5
−3
0
1
2
3
4
5
6
7
8

Understanding and Reducing Errors in Density Functional Theory, M. Kim et al., Phys. Rev. Lett. **111**, 073003 (2013).

$E_{\text{xc}}^{\text{LDA}}[n_{\text{accurate}}] \longrightarrow$ Very little improvement

i.e. It’s a “functional error”

Example: Stretched homunclear diatomics.

As opposed to:

$E_{\text{xc}}^{\text{LDA}}[n_{\text{accurate}}] \longrightarrow$ Significant improvement

“density-driven error”

Example: Electron affinities.

Ref.10 AW, J. Nafziger, K. Jiang, M-C.Kim, E. Sim, and K. Burke, *The Importance of Being Inconsistent*, Ann. Rev. Phys. Chem. **68**, 555 (2017).

Total error: $\Delta E = \overset{\text{Approximate}}{\tilde{E}} - \overset{\text{Exact}}{E} = \Delta E_F + \Delta E_D$

Functional error: $\Delta E_F = \tilde{F}[n] - F[n]$

Density-driven error:

$$\Delta E_D = \tilde{F}[\tilde{n}] - \tilde{F}[n] + \int d^3r \big(\tilde{n}(\mathbf{r}) - n(\mathbf{r})\big) v(\mathbf{r})$$

In “normal” calculations, $\Delta E_F >> \Delta E_D$

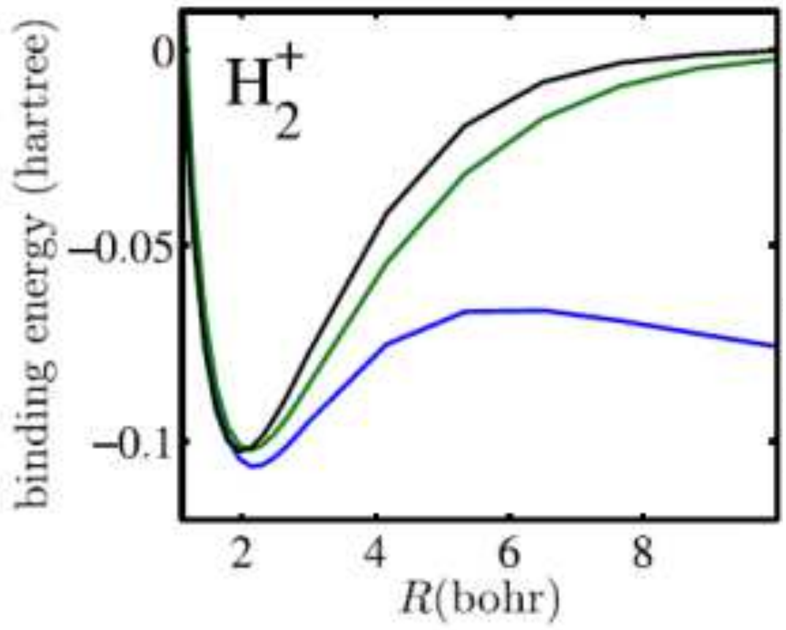
M. Kim et al., *Understanding and Reducing Errors in Density Functional Theory*, Phys. Rev. Lett. **111**, 073003 (2013).

M. Vuckovic et al., *Density Functional Analysis: The Theory of Density-Corrected DFT*, J. Chem. Theory Comput. **15**, 6636 (2019).

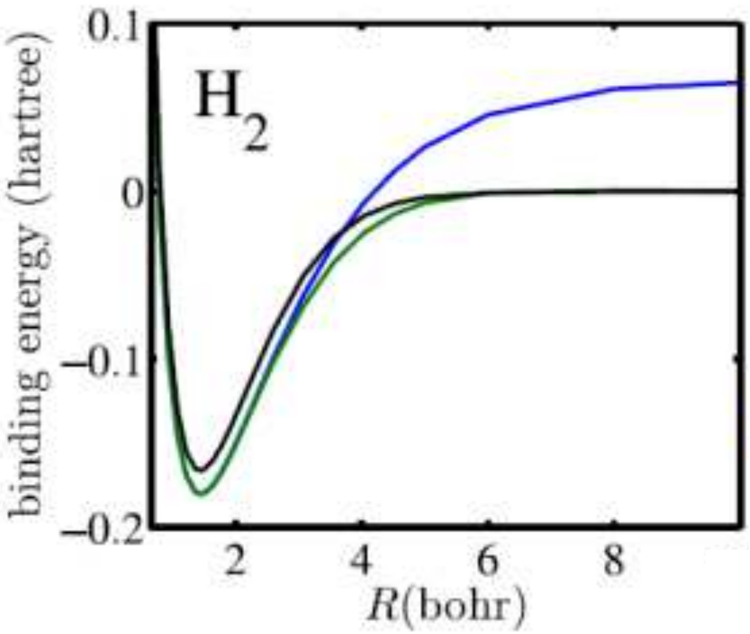
Outline

- Simplest possible examples of density functionals
- Chemical Potential
- Derivative Discontinuities
- **Key errors (self-interaction, delocalization, static-correlation)**

For detailed error analysis when stretching bonds, check Ref.9: Cohen, Mori-Sanchez, and Yang, Chem. Rev. (2012).



Delocalization error

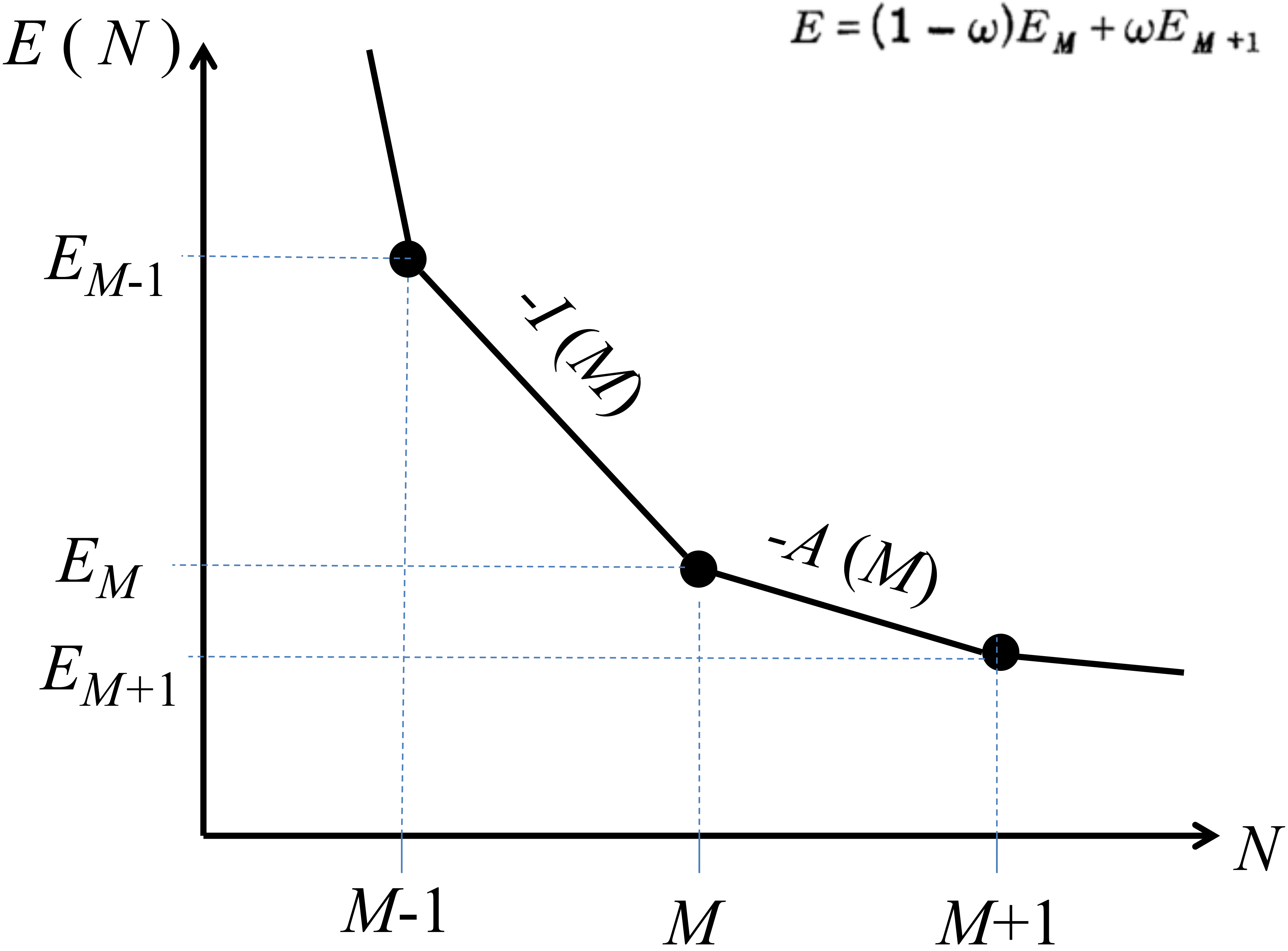


Static-correlation error

exact
LDA
OA-LDA

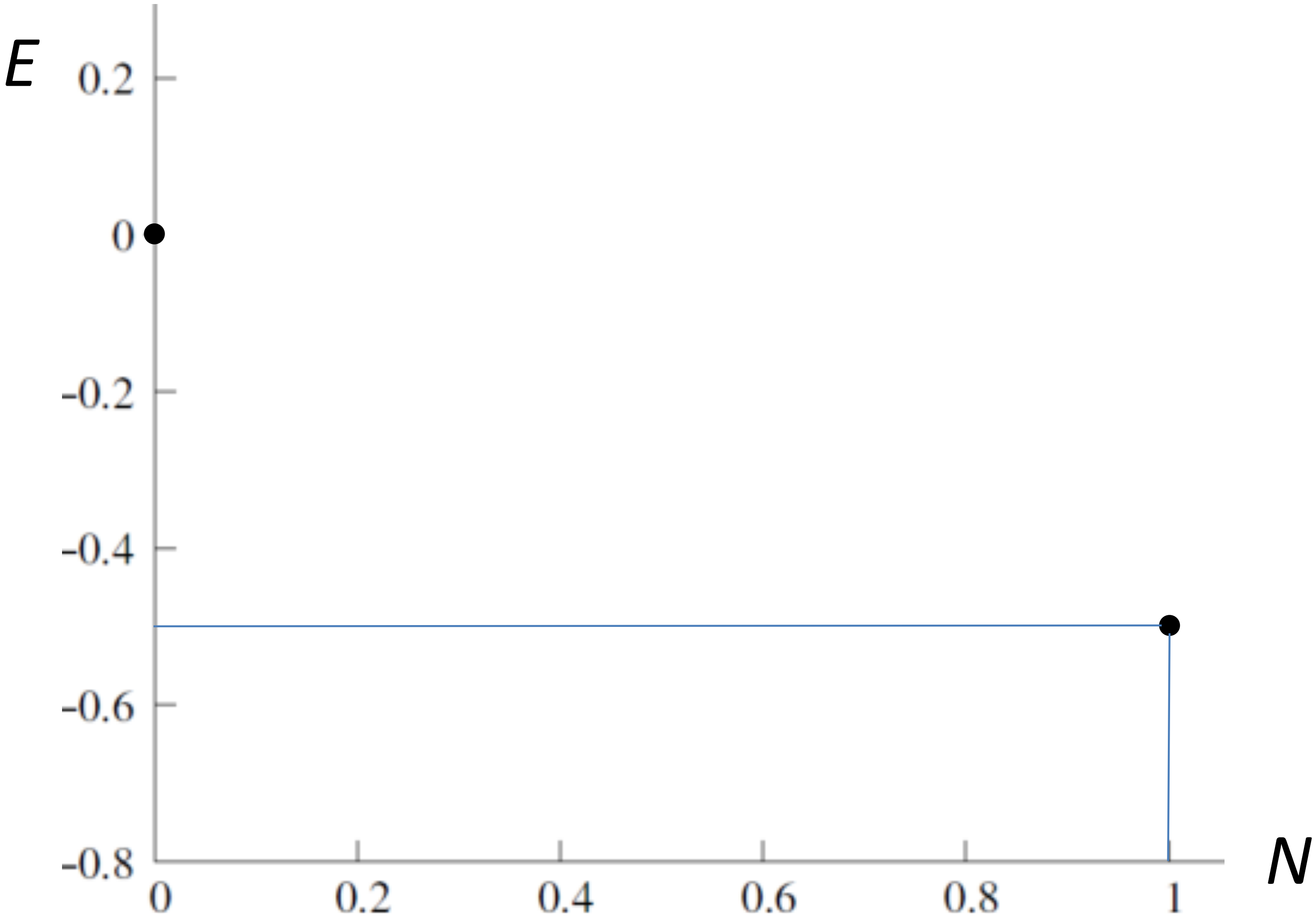
J. Nafziger and AW, JCP **143**, 234105 (2015).

$$E = (1 - \omega)E_M + \omega E_{M+1}$$

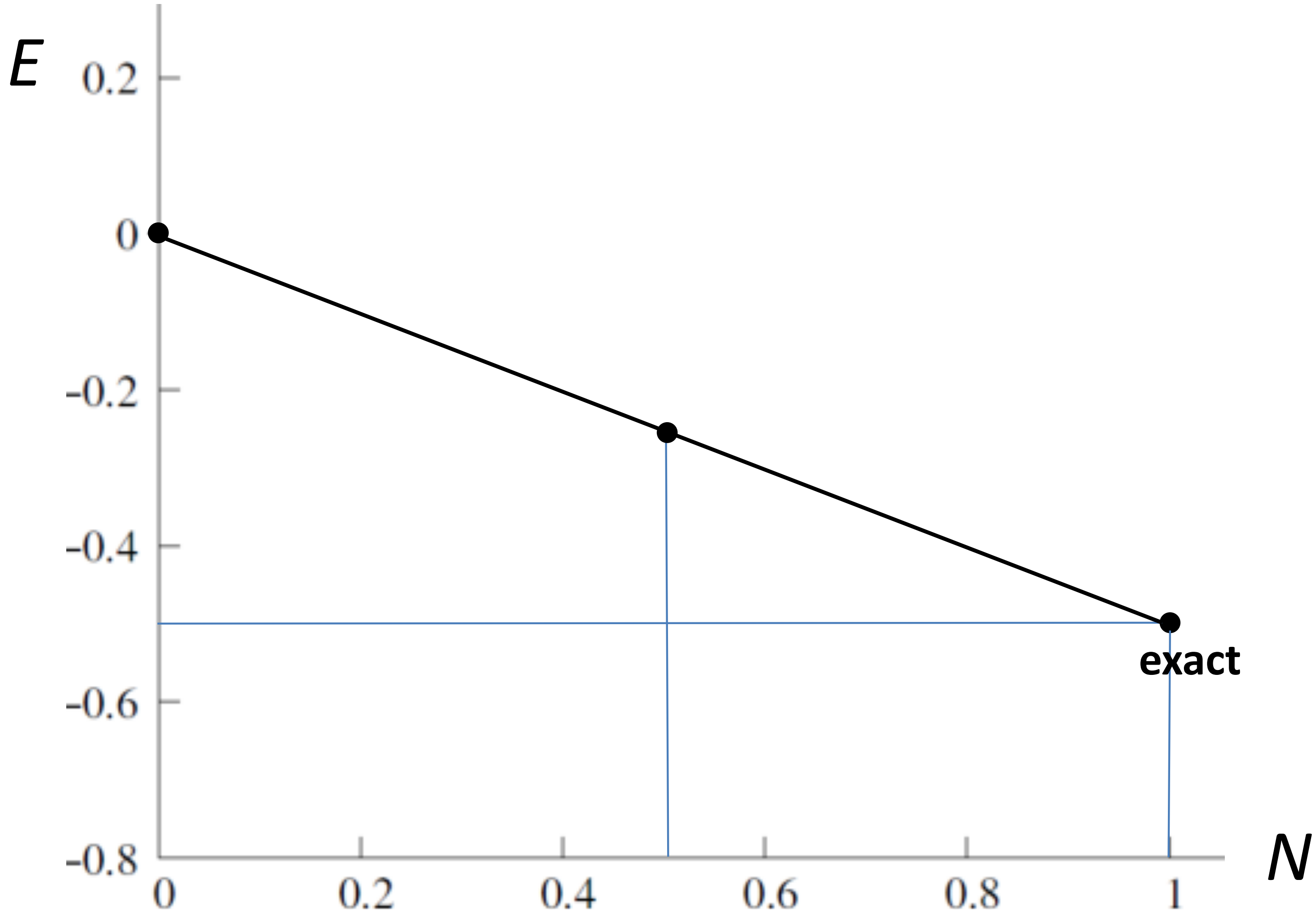


J.P. Perdew, R.G. Parr, M. Levy, J.L. Balduz, Phys. Rev. Lett. **49**, 1691 (1982).

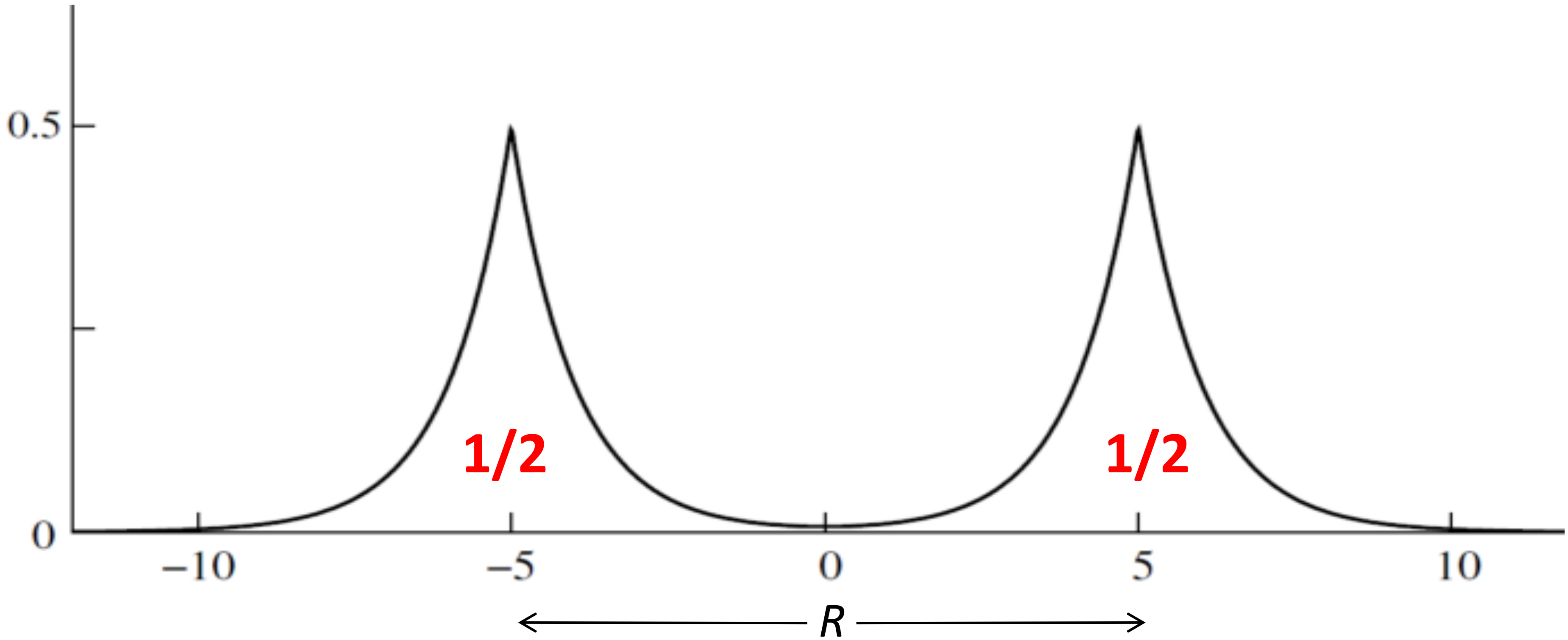
H atom



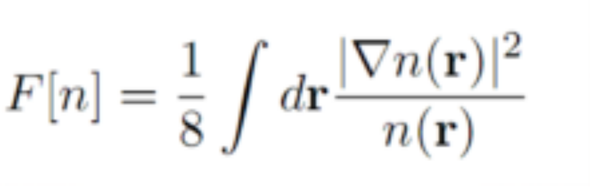
H atom



Stretched H_2^+



$E\ (R \to \infty) \longrightarrow E$ of H atom



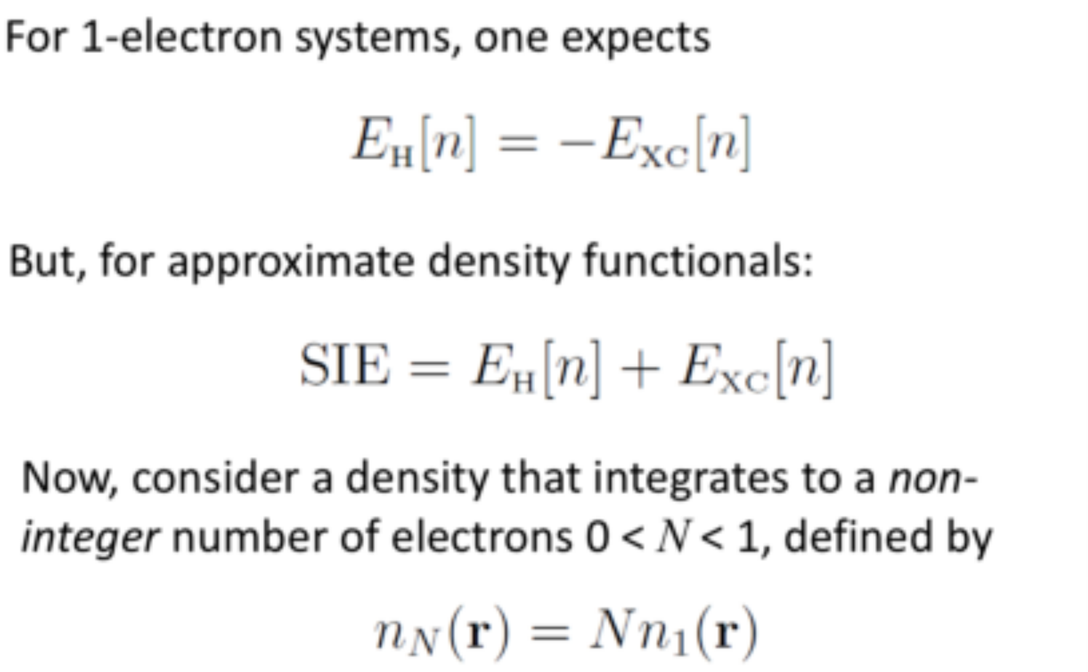
$$F[n] = \frac{1}{8}\int d\mathbf{r}\,\frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})}$$

Check linearity of the exact functional for (up to) 1 electron:

Define $n_N(\vec{r}) = N\, n(\vec{r})$

$$F[n_N] = N\, F[n]$$

$$E[n] = F[n] + \int d^3r\, v(\vec{r})\, n(\vec{r})$$



For 1-electron systems, one expects

$$E_{\mathrm{H}}[n] = -E_{\mathrm{XC}}[n]$$

But, for approximate density functionals:

$$\mathrm{SIE} = E_{\mathrm{H}}[n] + E_{\mathrm{XC}}[n]$$

Now, consider a density that integrates to a *non-integer* number of electrons 0 < N < 1, defined by

$$n_N(\mathbf{r}) = N n_1(\mathbf{r})$$

Since

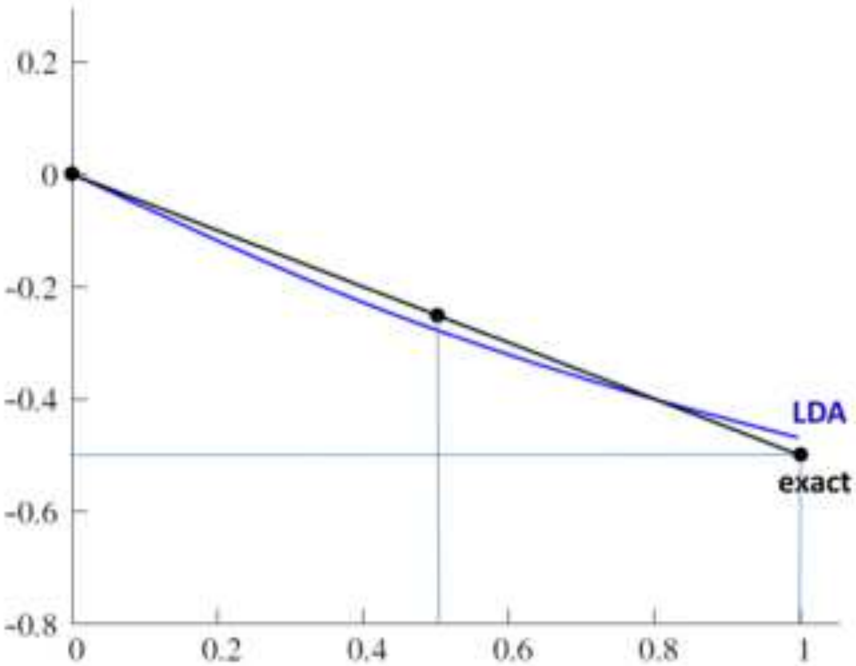
$$E_{\rm H}[n] = \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

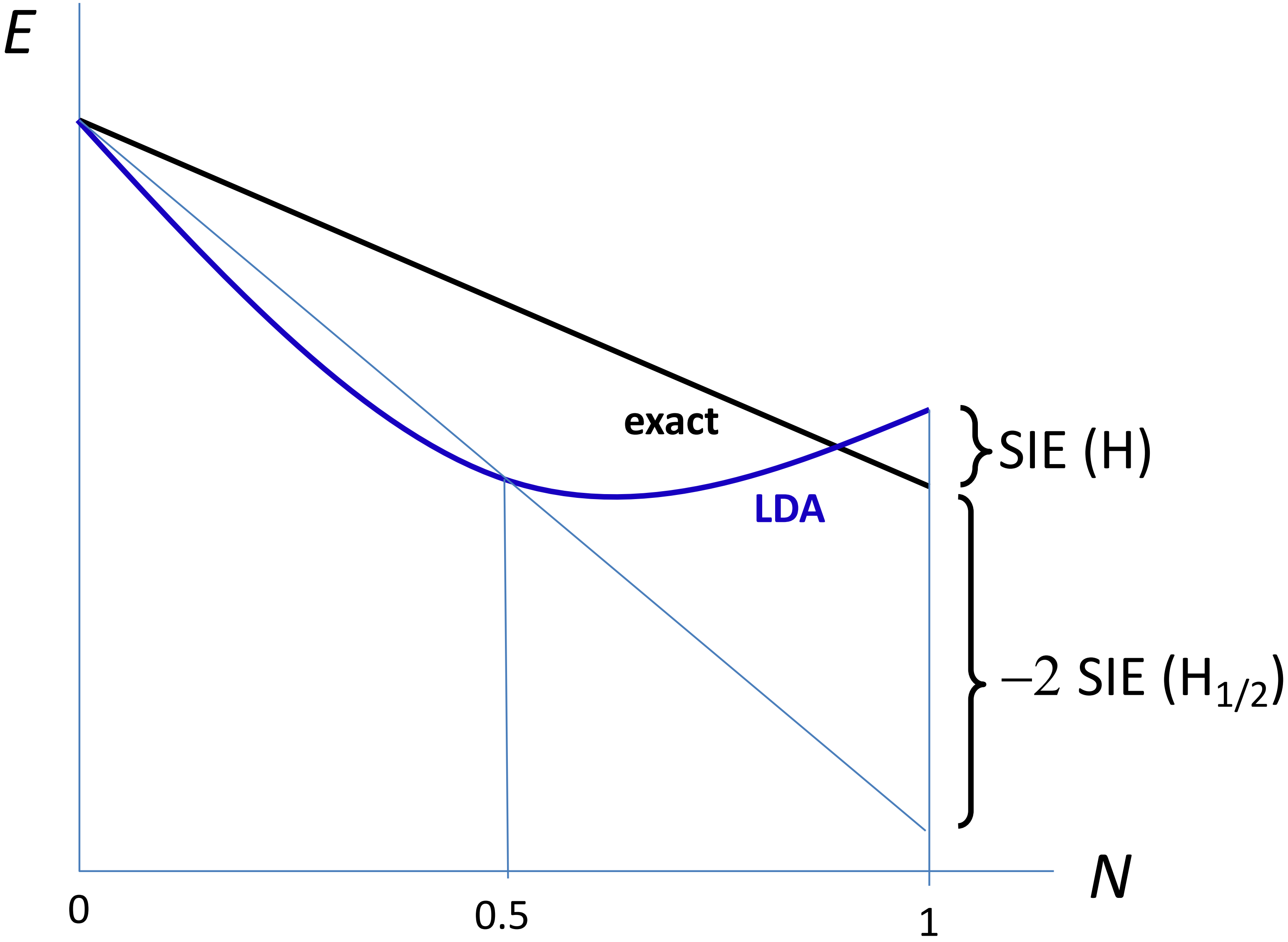
$$E_{\rm X}^{\rm LDA}[n] = A_{\rm X}\int d\mathbf{r}n^{4/3}(\mathbf{r})$$

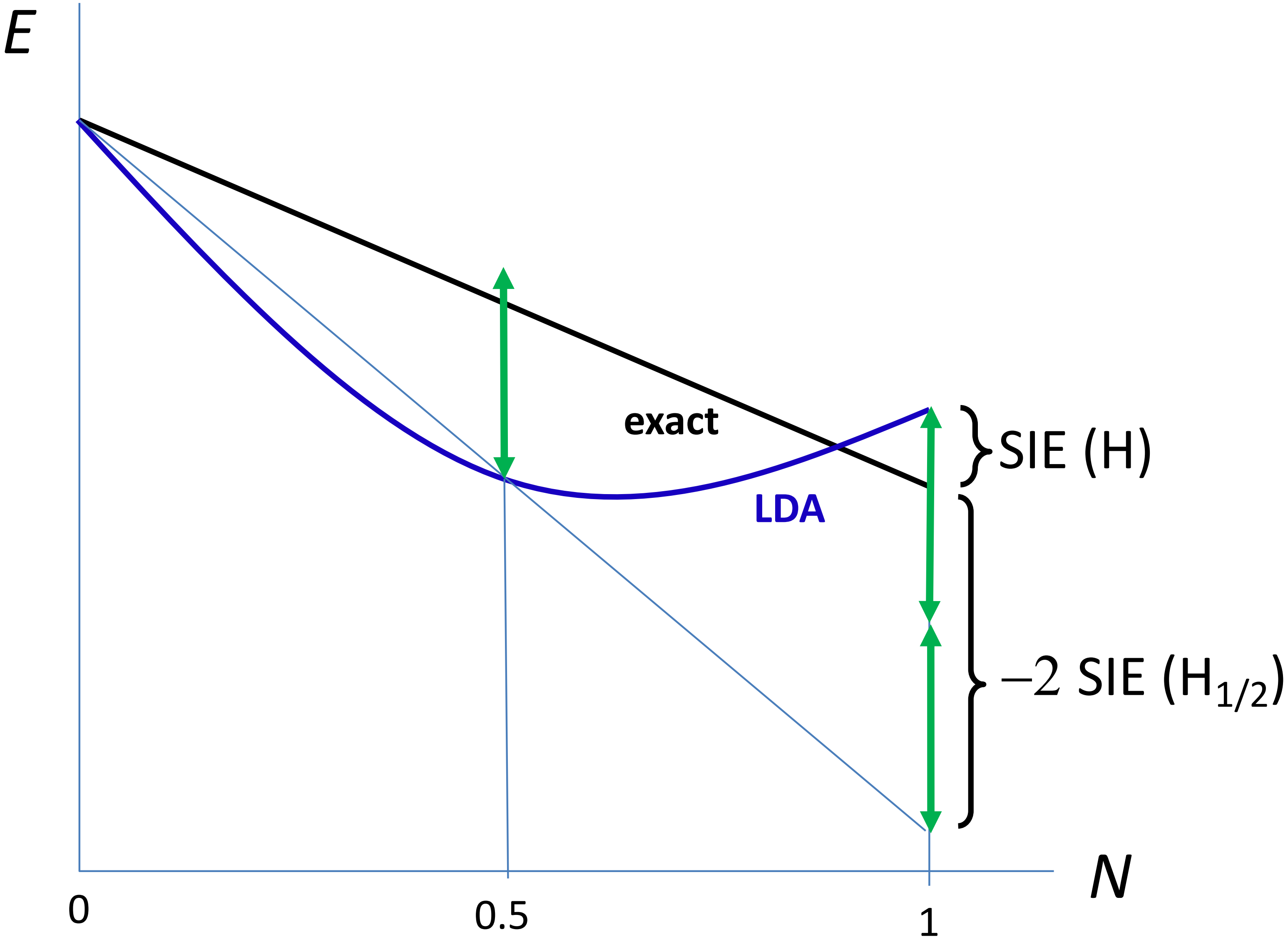
Then:

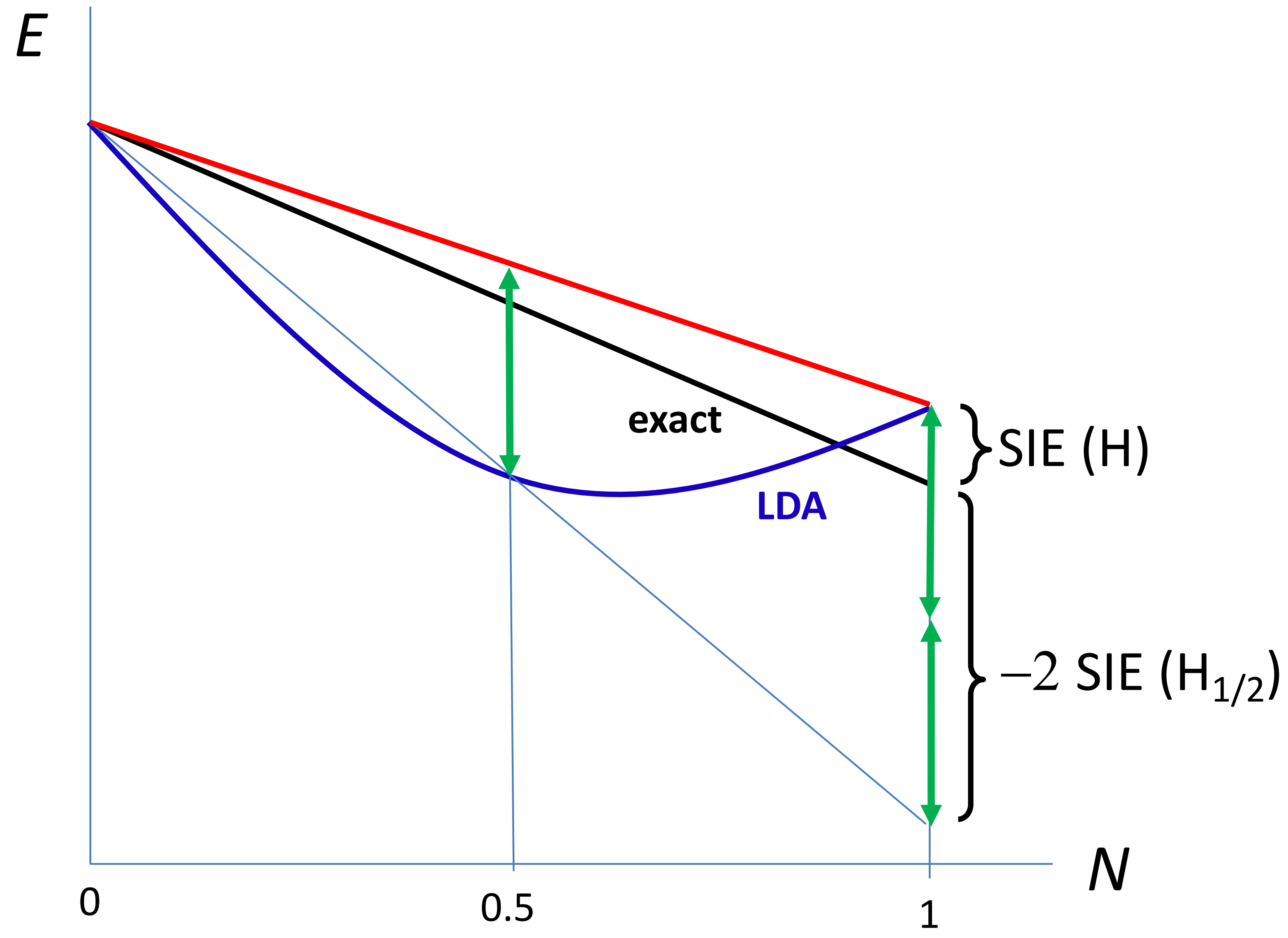
$$\overset{\rm LDA}{\rm SIE}(N) = \underset{\substack{\downarrow \\ N^2 E_{\rm H}[n_1]}}{E_{\rm H}[Nn_1]} + \underset{\substack{\downarrow \\ N^{4/3} E_{\rm X}[n_1]}}{E_{\rm XC}[Nn_1]}$$

But LDA is convex

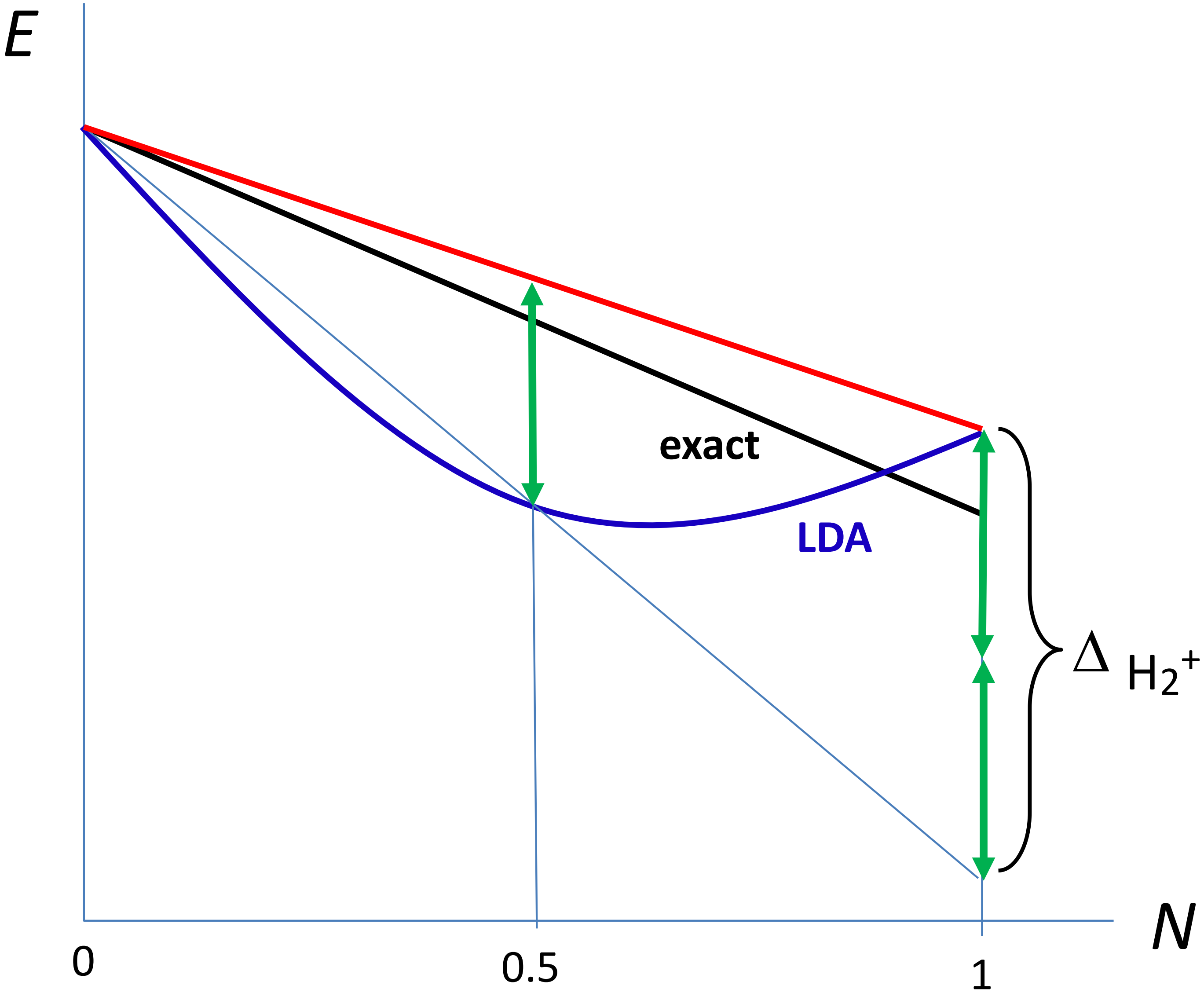



E
exact
LDA
SIE (H)
-2 SIE ($H_{1/2}$)
N
0
0.5
1

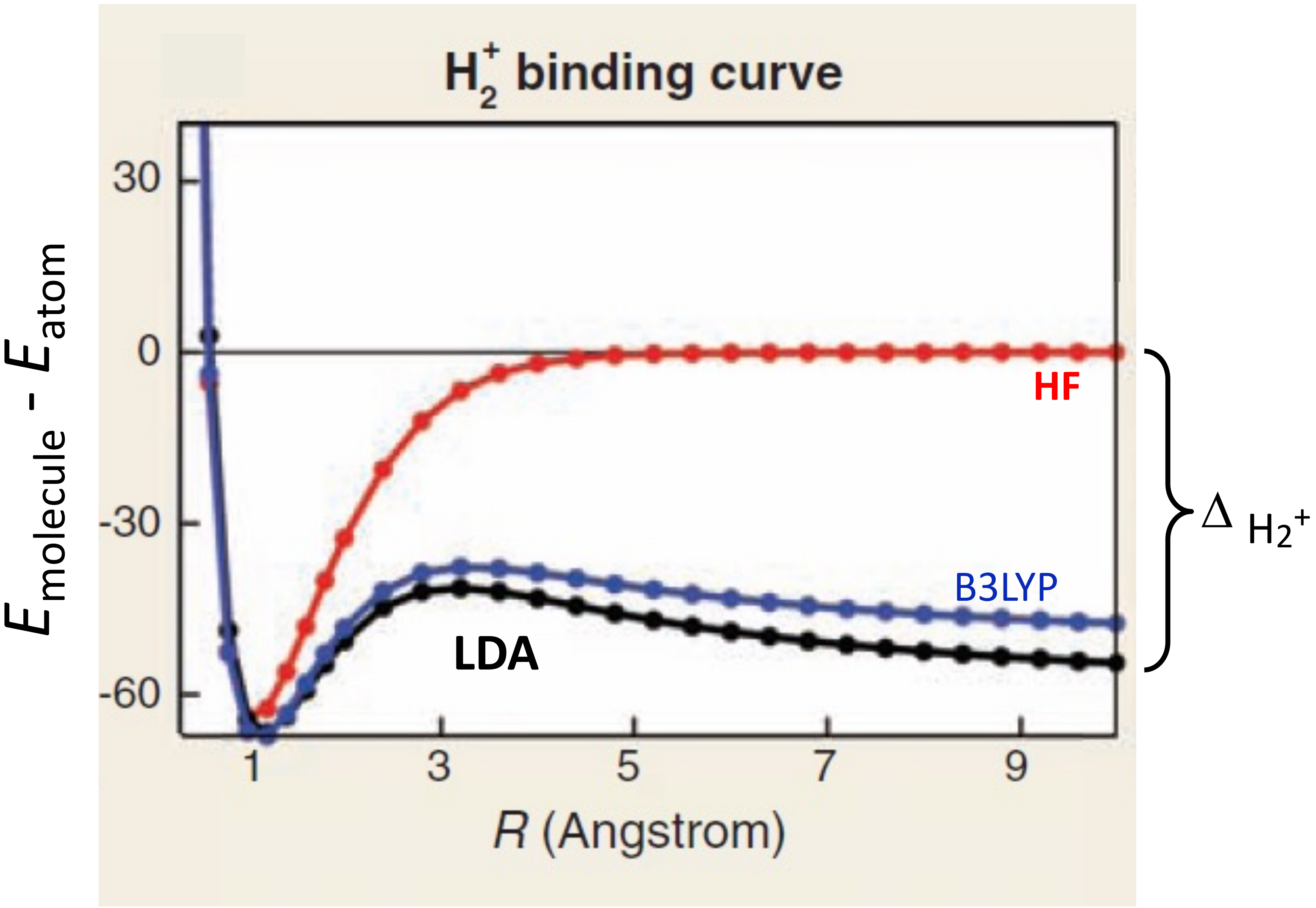

E
exact
LDA
SIE (H)
-2 SIE ($H_{1/2}$)
N
0
0.5
1



E
exact
LDA
SIE (H)
-2 SIE ($H_{1/2}$)
0
0.5
1
N



E
exact
LDA
Δ
H_2^+
N
0
0.5
1



Aron J. Cohen, Paula Mori-Sánchez and Weitao Yang

Science **321**, 792 (2008);

DOI: 10.1126/science.1158722

Approximate DFT calculations typically…

Underestimate:

- Energies of dissociating molecular ions
- Barriers of Chemical Reactions
- Band gaps of materials
- Charge transfer excitation energies

Overestimate:

- Binding energies of charge-transfer complexes
- Response to Electric fields

Aron J. Cohen, Paula Mori-Sánchez and Weitao Yang
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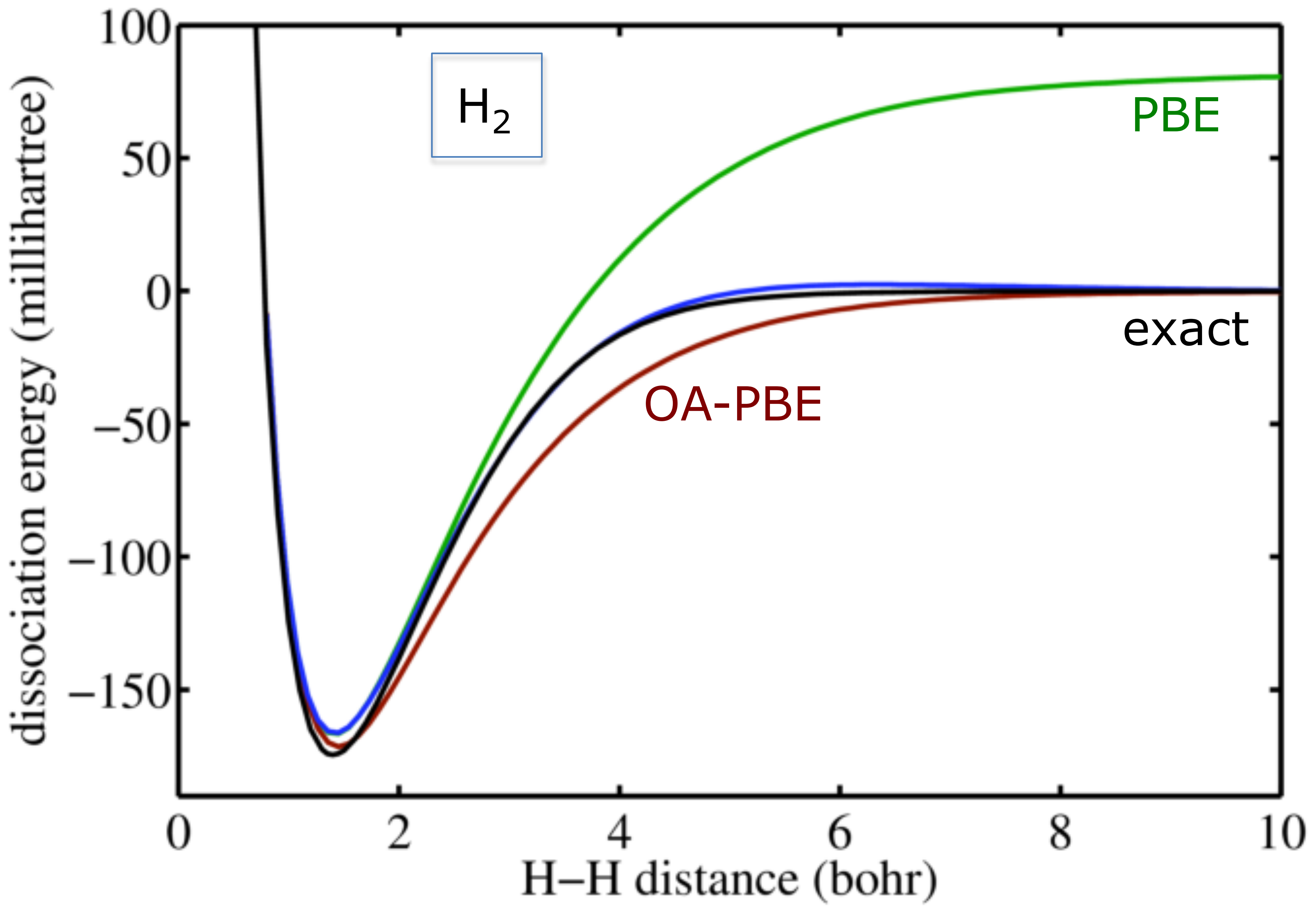
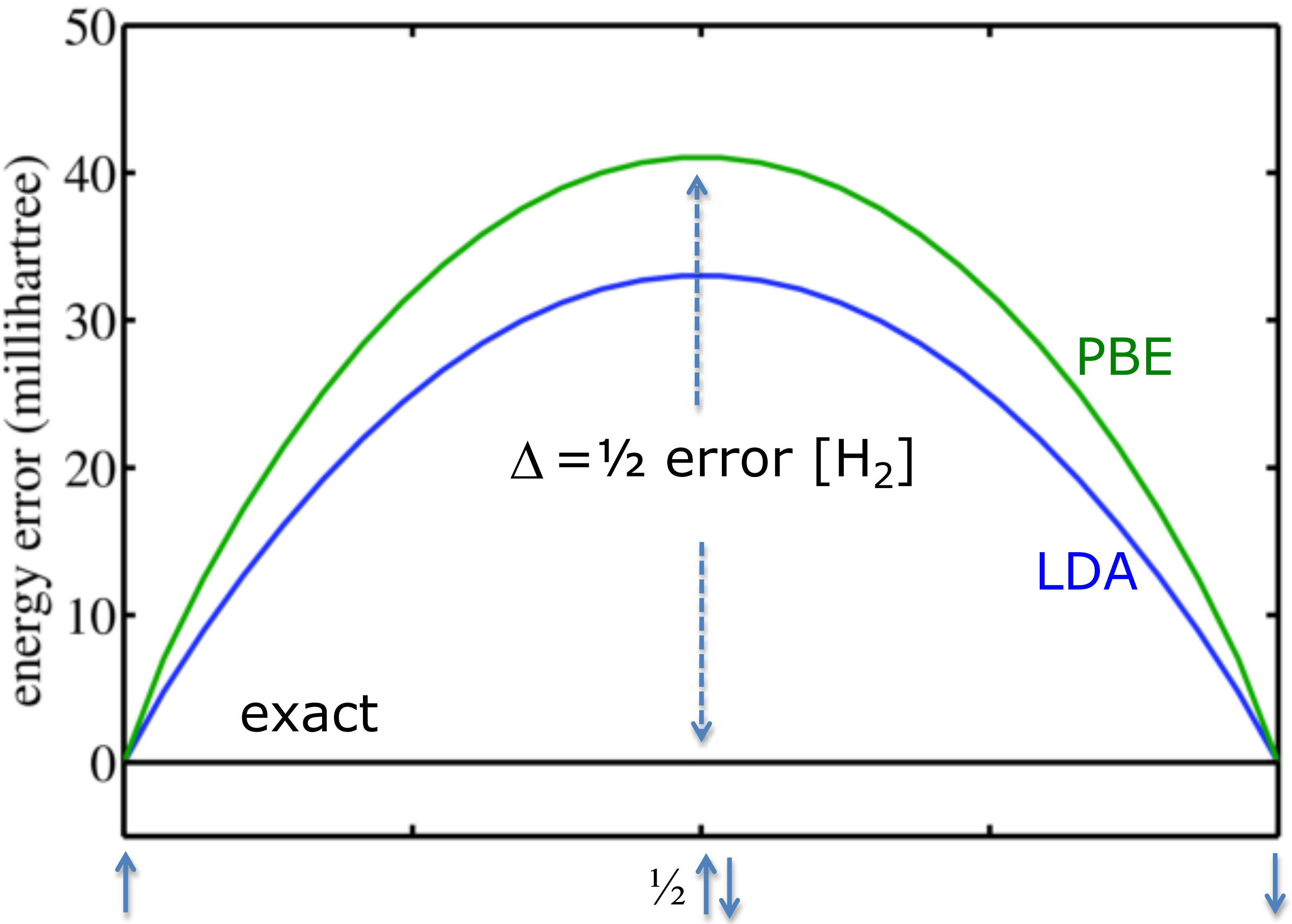
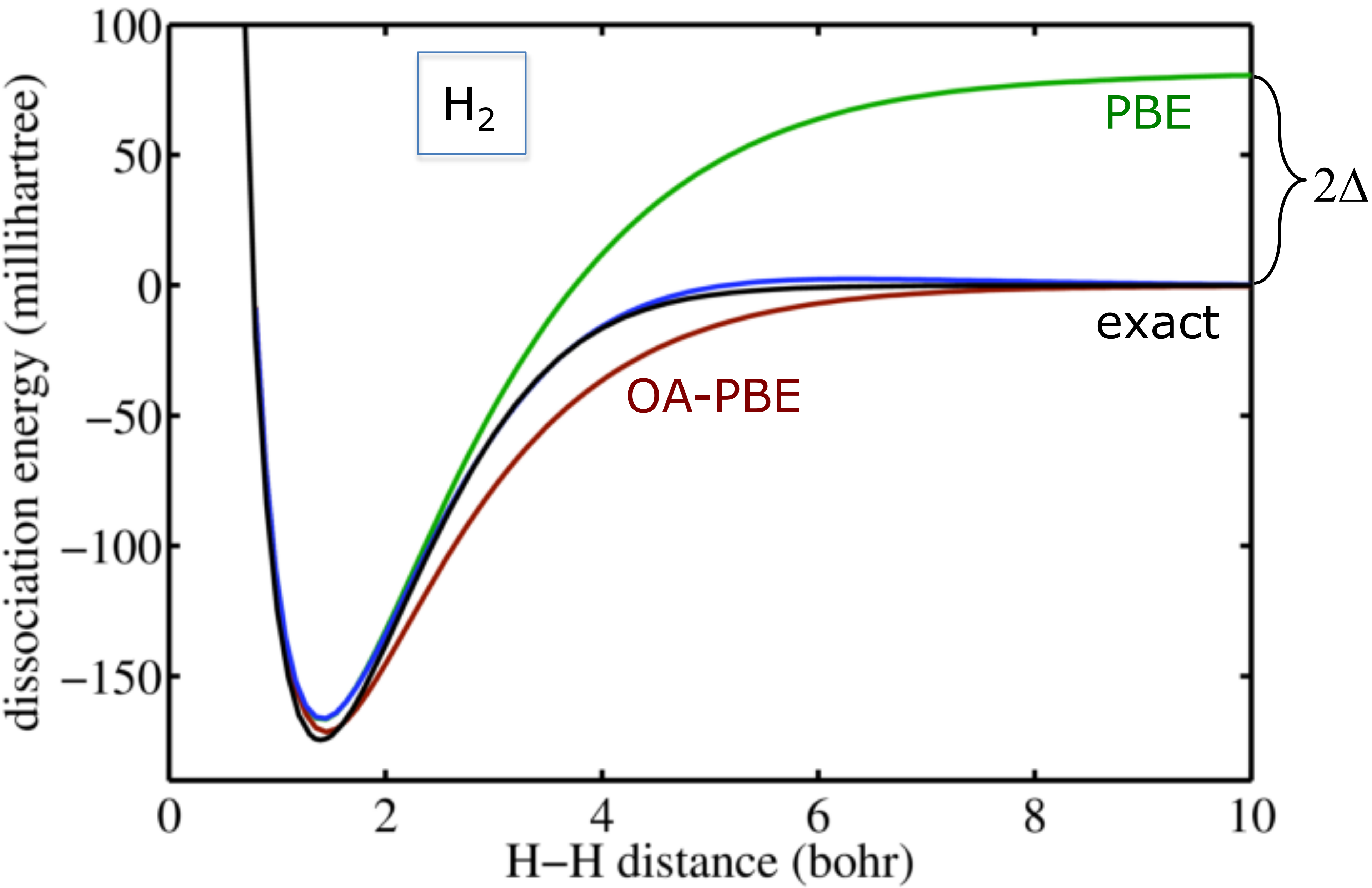


J. Nafziger and AW, JCP **143**, 234105 (2015).

Fractional Spins in the Hydrogen atom:



Static Correlation Error



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

FAQ and FHM:

#1: Since $F[n]$ is independent of the external potential, why not calculate F extremely accurately for one system and then use it for all others?
Misunderstood the meaning of "universal functional".

#2: What is the physical meaning of the Lagrange multiplier μ ?
That depends. Could be –I or could be -A

#3: I'm doing a band-structure calculation with a good semi-local functional. Why is my band-gap wrong?
Lack of derivative discontinuity in approximate functional.

#4: Do "good densities" imply "good energies" ?
Not necessarily.

#5: Which functional should I choose ?

Check out W. Koch and M.C. Holthausen: "A Chemist's Guide to Density Functional Theory", Wiley (2001).

K. Burke, Perspective on Density Functional Theory, J. Chem. Phys. **136**, 150901 (2012).

> “Clearly, when calculating a property to compare with experiment, one could keep trying functionals until agreement with the measured value is reached. Not only is this contrary to the entire spirit of DFT, it is certainly not first principles, and is the worst form of empiricism. The literature today is (mildly) infected with such calculations, and the existence of so many approximations, with so little guidance, makes it ever more difficult for non-specialists to separate the silver from the dross. Users should stick to the standard functionals (as most do, according to Fig. 1), or explain very carefully why not.”

K. Burke, Perspective on Density Functional Theory, J. Chem. Phys. **136**, 150901 (2012).

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That also depends. But after picking one, stick to it.