PHYSICS OF DENSITY FUNCTIONAL THEORY

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BASIC REFERENCES

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PHYS. REV. 140, A1133 (1965)

3. R.G. PARR & W. YANG
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(OXFORD, NY, 1989)

4. C. FIOLHAIS ET AL. (EDS.)
A PRIMER IN DENSITY FUNCTIONAL THEORY
(SPRINGER, BERLIN, 2003).

5. J.P. PERDEW & S. KURTH
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COULOMB SYSTEMS (IN REF. 4)

6. WEBSITE OF THE BURKE RESEARCH GROUP

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DFT BOOK

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7. J.P. PERDEW, R.G. PARR, M. LEVY, AND J.L. BALDUZ
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BRIEF HISTORY OF DFT

1928 THOMAS - FERMI THEORY

1930's HARTREE + HARTREE - FOCK

1950's SLATER'S LOCAL DENSITY APPROX. FOR EXCHANGE

1964 HOHENBERG-KOHN THEOREM

1965 KOHN-SHAM METHOD

1970's DFT DOMINATES CONDENSED MATTER PHYSICS.
WHY LOCAL APPROX'S WORK.

1980's + 1990's IMPROVED APPROX.'S

1984 RUNGE - GROSS THEOREM OF TD-DFT

1990's DFT STARTS TO DOMINATE QUANTUM CHEMISTRY

1998 NOBEL PRIZE IN CHEMISTRY:
WALTER KOHN + JOHN POPLE

SOME STANDARD DFT CODES :

FOR MOLECULES

- GAUSSIAN
- ADF
- TURBOMOLE
- DMOL

FOR SOLIDS

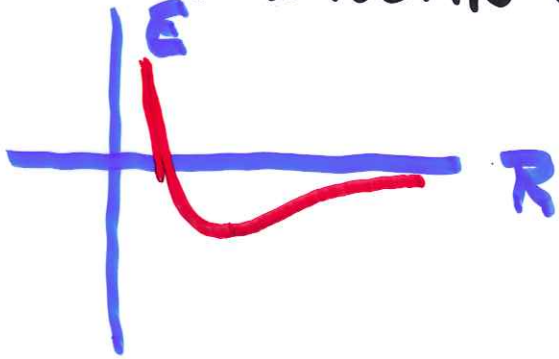
- VASP
- BAND
- WIEN
- AB INIT

ELECTRONIC STRUCTURE PROBLEM FOR ATOMS, MOLECULES, & SOLIDS

WHAT ATOMS, MOLECULES, & SOLIDS CAN EXIST, AND WITH WHAT PROPERTIES?

WHAT ARE THE GROUNDSTATE ENERGIES E AND ELECTRON DENSITIES $n(\vec{r})$?

WHAT ARE THE BOND LENGTHS + ANGLES?



WHAT ARE THE NUCLEAR VIBRATIONS?

HOW MUCH ENERGY IS NEEDED TO IONIZE THE SYSTEM, OR TO BREAK BONDS?

WAVEFUNCTION APPROACH

HAMILTONIAN FOR N ELECTRONS ($i = 1 \ldots N$) IN THE PRESENCE OF EXTERNAL POTENTIAL $v(\vec{r})$:

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \sum_i v(\vec{r}_i)$$

$$\hat{T} = \sum_i -\frac{1}{2} \nabla_i^2$$

$$\hat{V}_{ee} = \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{|\vec{r}_i - \vec{r}_j|} .$$

OFTEN $v(\vec{r}) = \sum_B \frac{-Z_B}{|\vec{r} - \vec{R}_B|}$

= ELECTRON-NUCLEUS ATTRACTION,

AND E INCLUDES ALSO

$$\frac{1}{2} \sum_B \sum_{\gamma \neq B} \frac{Z_B Z_\gamma}{|\vec{R}_B - \vec{R}_\gamma|}$$

= NUCLEUS-NUCLEUS REPULSION.

SCHRÖDINGER EQUATION FOR STATIONARY STATES $\hat{H}\Psi = E\Psi$

$$\Psi = \Psi(\vec{r}_1 \sigma_1, \vec{r}_2 \sigma_2, \ldots \vec{r}_N \sigma_N)$$

Ψ IS NORMALIZED: $\langle \Psi | \Psi \rangle = 1$,

AND ANTISYMMETRIC:

$$\Psi(\ldots \vec{r}_i \sigma_i \ldots \vec{r}_j \sigma_j \ldots) = -\Psi(\ldots \vec{r}_j \sigma_j \ldots \vec{r}_i \sigma_i \ldots)$$

$E \to \Delta E$

$$n(\vec{r}) = N \sum_{\sigma_1} \ldots \sum_{\sigma_N} \int d^3 r_2 \ldots d^3 r_N \left| \Psi(\vec{r}\,\sigma_1, \vec{r}_2 \sigma_2, \ldots \vec{r}_N \sigma_N) \right|^2$$

$n(\vec{r})\, d^3 r$ = AVERAGE NUMBER OF ELECTRONS IN VOLUME ELEMENT $d^3 r$ AT $\vec{r}$.

$h[\Psi] \equiv \langle \Psi | \hat{A} | \Psi \rangle$

IS A FUNCTIONAL:

A RULE THAT ASSIGNS A NUMBER h TO EVERY FUNCTION Ψ.

WAVEFUNCTION VARIATIONAL PRINCIPLE:

THE EXTREMA OF $h[\Psi]$ ARE THE STATIONARY STATES, AND THE ABSOLUTE MINIMUM IS THE GROUND STATE.

WAVEFUNCTIONS ARE NEVER USED FOR LARGE ELECTRON NUMBER N!

WHY NOT MANY-ELECTRON WAVE FUNCTIONS?

IMAGINE A GRID OF M POINTS IN POSITION SPACE FOR EACH ELECTRON. WE MUST THEN COMPUTE & STORE M^N VALUES OF Ψ. (KOHN)

LET $M = 10^2$ (NOT REALLY ENOUGH).

FOR $N=2$, $M^N = 10^4$ IS OK.

FOR $N=10$, $M^N = 10^{20}$ IS NOT OK.

AVOIDING GRIDS, ONE CAN STUDY AT MOST (AND AT GREAT EXPENSE) 10 TO 100 ELECTRONS.

THE DENSITY $n(\vec{r})$ HOWEVER WOULD REQUIRE COMPUTING & STORING ONLY M VALUES.

HOHENBERG-KOHN THEOREM 1964:

CENTRAL THEOREM OF DFT

(1) THERE EXISTS A FUNCTIONAL $F[n]$ OF THE ELECTRON DENSITY, SUCH THAT THE GS ENERGY AND DENSITY FOR N ELECTRONS IN THE PRESENCE OF EXTERNAL POTENTIAL $v(\vec{r})$ IS

$$E_{GS} = \min_{n} \left\{ F[n] + \int d^3r\, v(\vec{r})\, n(\vec{r}) \right\}.$$

THE MINIMUM IS TAKEN OVER ALL POSITIVE $n(\vec{r})$ SUCH THAT $\int d^3r\, n(\vec{r}) = N$.

$F[n]$ IS UNIVERSAL (INDEPENDENT OF v)

THE PROBLEM IS TO FIND (APPROXIMATE) THE FUNCTIONAL $F[n]$.

(2) THE EXTERNAL POTENTIAL $v(\vec{r})$ AND HENCE THE HAMILTONIAN $\hat{H}$ ARE DETERMINED TO WITHIN AN ADDITIVE CONSTANT BY $n(\vec{r})$.

PROOF BY LEVY CONSTRAINED SEARCH '79

$$E_{GS} = \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{ee} + \sum_i v(\vec{r}_i) | \Psi \rangle$$

$$= \min_{n} \min_{\Psi \to n} \left\{ \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int d\vec{r}\, v(\vec{r}) n(\vec{r}) \right\}$$

$$(1) \quad = \min_{n} \left\{ F[n] + \int d\vec{r}\, v(\vec{r}) n(\vec{r}) \right\}$$

$$F[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$$

$$= \langle \Psi_n | \hat{T} + \hat{V}_{ee} | \Psi_n \rangle$$

Ψ_n = THAT WAVEFUNCTION YIELDING DENSITY $n(\vec{r})$ THAT MINIMIZES $\langle \hat{T} + \hat{V}_{ee} \rangle$

EULER EQUATION FOR $n(\vec{r})$:

$$\delta \left\{ F[n] + \int d^3r\, n(\vec{r})\, v(\vec{r}) - \mu \int d^3r\, n(\vec{r}) \right\} = 0$$

$$\left.\begin{aligned} &\frac{\delta F}{\delta n(\vec{r})} + v(\vec{r}) - \mu = 0 \\ (2)\quad &v(\vec{r}) = \mu - \frac{\delta F}{\delta n(\vec{r})} \end{aligned}\right\} \text{FOR GS } n(\vec{r})$$

FUNCTIONAL DERIVATIVE $\frac{\delta F}{\delta n(\vec{r})}$:

$$\delta F = \int d^3r \left(\frac{\delta F}{\delta n(\vec{r})} \right) \delta n(\vec{r}) .$$

EX: $E_x^{LDA}[n] = -C \int d^3r\, n^{4/3}(\vec{r})$

$$\delta E_x^{LDA}[n] = -C \int d^3r\, \frac{4}{3} n^{1/3}(\vec{r})\, \delta n(\vec{r})$$

$$\frac{\delta E_x^{LDA}}{\delta n(\vec{r})} = -\frac{4}{3} C\, n^{1/3}(\vec{r})$$

THE CONSTRAINED SEARCH IS FOR UNDERSTANDING, NOT FOR CALCULATING!

THE EXACT F[n] REQUIRES A CONSTRAINED SEARCH OVER N-ELECTRON WAVEFUNCTIONS, WHICH IS IMPRACTICAL.

APPROXIMATIONS FOR F[n] THAT ARE EXPLICIT FUNCTIONALS OF $n(\vec{r})$ ARE TOO CRUDE TO BE VERY USEFUL. (E.G., TF THEORY)

1965: THE KOHN-SHAM SCHEME INTRODUCES ORBITALS THAT ARE IMPLICIT FUNCTIONALS OF THE DENSITY, AND CALCULATES THE BIGGEST PART OF F[n] EXACTLY* FROM THESE ORBITALS.

KOHN-SHAM NON-INTERACTING SYSTEM :

A FICTIONAL NON INTERACTING GROUND STATE Φ_n (USUALLY A SINGLE SLATER DETERMINANT) WITH THE SAME DENSITY $n(\vec{r})$ AND CHEMICAL POTENTIAL AS THE PHYSICAL INTERACTING GROUND STATE Ψ_n.

$$\hat{H}_s = \hat{T} + \sum_i v_s(\vec{r}_i)$$

s = single-particle

$$\hat{H}_s \Phi_n = E_s \Phi_n$$

Φ_n = THAT NONINTERACTING WAVE FUNCTION YIELDING DENSITY $n(\vec{r})$ AND MINIMIZING $\langle \hat{T} \rangle$.

NON-INTERACTING KINETIC ENERGY

$$T_s[n] = \langle \Phi_n | \hat{T} | \Phi_n \rangle$$

$$F[n] = \langle \Psi_n | \hat{T} + \hat{V}_{ee} | \Psi_n \rangle$$

$$= \langle \Phi_n | \hat{T} + \hat{V}_{ee} | \Phi_n \rangle + E_c[n]$$

CORRELATION ENERGY

$$E_c[n] = \langle \Psi_n | \hat{T} + \hat{V}_{ee} | \Psi_n \rangle - \langle \Phi_n | \hat{T} + \hat{V}_{ee} | \Phi_n \rangle$$

$$\leq 0.$$

$$\langle \Phi_n | \hat{V}_{ee} | \Phi_n \rangle = U[n] + E_x[n]$$

HARTREE ELECTROSTATIC ENERGY

$$U[n] = \frac{1}{2} \int d\vec{r} \int d\vec{r}\,' \frac{n(\vec{r})\, n(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}$$

EXCHANGE ENERGY $E_x[n]$

$$F[n] = \underbrace{T_s[n] + U[n]}_{\text{TREATED EXACTLY}} + \underbrace{E_{xc}[n]}_{\substack{\text{SOME APPROX. FOR} \\ E_x + E_c \\ \text{(OR AT LEAST FOR } E_c\text{)}}}$$

EULER EQUATIONS

$$\frac{\delta T_s}{\delta n(\vec{r})} + v_s(\vec{r}) = \mu$$

$$\frac{\delta T_s}{\delta n(\vec{r})} + \frac{\delta U}{\delta n(\vec{r})} + \frac{\delta E_{xc}}{\delta n(\vec{r})} + v(\vec{r}) = \mu$$

} SAME SOLUTION

$$v_s(\vec{r}) = v(\vec{r}) + \int d^3r' \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + v_{xc}([n];\vec{r})$$

$$v_{xc}([n];\vec{r}) = \frac{\delta E_{xc}}{\delta n(\vec{r})}$$

SELFCONSISTENT KOHN-SHAM SCHEME

$$\left[-\tfrac{1}{2}\nabla^2 + v(\vec{r}) + \int d^3r' \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + v_{xc}([n];\vec{r})\right]\psi_\alpha(\vec{r}) = \varepsilon_\alpha \psi_\alpha(\vec{r})$$

$$n(\vec{r}) = \sum_\alpha^{occup} |\psi_\alpha(\vec{r})|^2$$

$$T_s[n] = \sum_\alpha^{occup} \int d^3r\, \psi_\alpha^*(\vec{r}) \left(-\tfrac{1}{2}\nabla^2\right) \psi_\alpha(\vec{r})$$

THE KOHN-SHAM ORBITALS $\psi_\alpha(\vec{r})$ ARE IMPLICIT FUNCTIONALS OF $n(\vec{r})$.

SPIN DENSITY FUNCTIONAL THEORY (SDFT)

GENERALIZATIONS

$v(\underline{r}) \rightarrow v_\uparrow(\underline{r}), v_\downarrow(\underline{r})$

(MAGNETIC FIELD COUPLING TO ELECTRON SPIN)

$n(\underline{r}) \rightarrow n_\uparrow(\underline{r}), n_\downarrow(\underline{r})$

EVEN WHEN $v_\uparrow(\underline{r}) = v_\downarrow(\underline{r})$, WE CAN HAVE $n_\uparrow(\underline{r}) \neq n_\downarrow(\underline{r})$ IN AN OPEN-SHELL SYSTEM. IN THAT CASE, THE EXTRA INFORMATION IN $n_\uparrow(\underline{r}), n_\downarrow(\underline{r})$ IMPROVES THE ACCURACY OF APPROXIMATIONS FOR E_{xc}. MOST DFT CALCULATIONS ARE SDFT, BUT $\uparrow, \downarrow$ WILL BE SUPPRESSED FOR NOTATIONAL SIMPLICITY.

EXCHANGE-CORRELATION ENERGY *

$$E_{xc}[n] \leq 0$$

OR

$$E_{xc}[n_\uparrow, n_\downarrow] \leq 0$$

NATURE'S GLUE

ANALOGY BETWEEN ELECTRONS AND SHOPPERS IN A MALL

* A SMALL PIECE OF THE ENERGY AMENABLE FOR LOCAL OR SEMI-LOCAL APPROXIMATIONS (ESPECIALLY X+C TOGETHER!

COUPLING CONSTANT INTEGRAL FOR E_{xc}

LANGRETH + PERDEW 1975

$$\hat{H}_\lambda = \hat{T} + \lambda \hat{V}_{ee} + \sum_i v_\lambda(\vec{r}_i)$$

ADJUST $v_\lambda(\vec{r})$ TO HOLD THE GS DENSITY FIXED AT ITS $\lambda = 1$ VALUE.

$\lambda = 1$: REAL INTERACTING SYSTEM

$$v_\lambda(\vec{r}) = v(\vec{r}).$$

$\lambda = 0$: KOHN-SHAM NON-INTERACTING SYSTEM

Ψ_n^λ = THAT WAVEFUNCTION YIELDING DENSITY $n(\vec{r})$ THAT MINIMIZES $\langle \hat{T} + \lambda \hat{V}_{ee} \rangle$.

$$\Psi_n^1 = \Psi_n, \quad \Psi_n^0 = \Phi_n$$

$$E_{xc}[n] = \langle \Psi_n | \hat{T} + \hat{V}_{ee} | \Psi_n \rangle - \langle \Phi_n | \hat{T} | \Phi_n \rangle - U[n]$$

$$= \langle \Psi_n^\lambda | \hat{T} + \lambda \hat{V}_{ee} | \Psi_n^\lambda \rangle \Big|_{\lambda=0}^{1} - U[n]$$

$$= \int_0^1 d\lambda \frac{d}{d\lambda} \langle \Psi_n^\lambda | \hat{T} + \lambda \hat{V}_{ee} | \Psi_n^\lambda \rangle - U[n]$$

$$= \int_0^1 d\lambda \langle \Psi_n^\lambda | \hat{V}_{ee} | \Psi_n^\lambda \rangle - U[n]$$

BY HELLMANN-FEYNMAN

$$\langle \Psi_n^\lambda | \hat{V}_{ee} | \Psi_n^\lambda \rangle = \frac{1}{2} \int d^3r \int d^3r' \frac{\rho_2^\lambda(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|}$$

WHERE

$$\rho_2^\lambda(\vec{r}, \vec{r}') = N(N-1) \sum_{\sigma_1} \cdots \sum_{\sigma_N} \int d^3r_3 \cdots d^3r_N \, |\Psi_n^\lambda(\vec{r}\,\sigma_1, \vec{r}'\sigma_2, \vec{r}_3\sigma_3 \cdots \vec{r}_N\sigma_N)|^2$$

= TWO-PARTICLE DENSITY MATRIX

$\rho_2(\vec{r},\vec{r}')$ = JOINT PROBABILITY DENSITY

$= n(\vec{r})\left[n(\vec{r}') + n_{xc}(\vec{r},\vec{r}')\right]$

$\int d^3r \int d^3r' \rho_2(\vec{r},\vec{r}') = N(N-1)$

$\int d^3r \int d^3r' n(\vec{r})\, n(\vec{r}') = N(N)$

so $\int d^3r'\, n_{xc}(\vec{r},\vec{r}') = -1$ SUM RULE

$n_{xc}(\vec{r},\vec{r}')$ = DENSITY AT $\vec{r}'$ OF THE XC HOLE AROUND AN ELECTRON AT $\vec{r}$. AROUND AN ELECTRON AT $\vec{r}$, ONE ELECTRON IS MISSING FROM THE SPACE $\vec{r}' \neq \vec{r}$. (SHOPPERS IN A MALL.)

$$E_{xc}[n] = \int_0^1 d\lambda\, \frac{1}{2} \int d^3r \int d^3r'\, n(\vec{r})\, \frac{n_{xc}(\vec{r},\vec{r}')}{|\vec{r}-\vec{r}'|}$$

REVIEW

THE NUMBER OF VALUES NEEDED FOR N ELECTRONS ON A 3D GRID OF M $\propto$ N POINTS

FOR ELECTRON DENSITY : $M \propto N$

(ORDER-N METHOD)

FOR N KOHN-SHAM SPIN ORBITALS:

$M \cdot N \propto N^2$

FOR A CORRELATED N-ELECTRON WAVEFUNCTION : M^N

REAL CALCULATIONS USE A BASIS SET TO IMPROVE EFFICIENCY.

IMPORTANCE OF THE HOHENBERG-KOHN AND KOHN-SHAM EXISTENCE THEOREMS, & THE CONSTRAINED SEARCH:

KNOWING THAT EXACT DENSITY- AND ORBITAL FUNCTIONALS EXIST MOTIVATES US TO LOOK FOR GOOD APPROXIMATIONS TO THEM, AND GUIDES US IN THIS SEARCH.

THE EXCHANGE-CORRELATION ENERGY $E_{xc}[n]$ IS "NATURE'S GLUE".

COUPLING CONSTANT INTEGRAL FOR $E_{xc}[n]$

$$E_{xc}[n] = \frac{1}{2}\int d^3r\, n(\vec{r}) \int d^3r' \frac{n_{xc}(\vec{r},\vec{r}')}{|\vec{r}'-\vec{r}|}$$

$$n_{xc}(\vec{r},\vec{r}') = \int_0^1 d\lambda\, n_{xc}^{\lambda}(\vec{r},\vec{r}')$$

$n_{xc}(\vec{r},\vec{r}')$ = DENSITY AT $\vec{r}'$ OF THE XC HOLE AROUND AN ELECTRON AT $\vec{r}$. (LIKE THE "PERSONAL SPACE" AROUND A SHOPPER.)

SUM RULES

$$\int d^3r'\, n_x(\vec{r},\vec{r}') = -1$$

$$\int d^3r'\, n_c(\vec{r},\vec{r}') = 0$$

COUPLING CONSTANT INTEGRAL FOR $E_{xc}[n]$ + FLUCTUATION-DISSIPATION THEOREM

($n_{xc}(\vec{r},\vec{r}')$ FROM $\chi(\vec{r},\vec{r}',\omega)$)

→ RPA IN A DENSITY-FUNCTIONAL CONTEXT

(LANGRETH & PERDEW 1976)

E_x CAN BE EXPRESSED AS A FOCK INTEGRAL OF OCCUPIED ORBITALS:

$$n_x(\vec{r},\vec{r}') = n_{xc}^{\lambda=0}(\vec{r},\vec{r}')$$

$$= -\frac{1}{n(\vec{r})} \sum_i |\rho_i(\vec{r},\vec{r}')|^2$$

WHERE $\rho_i(\vec{r},\vec{r}') = \sum_\alpha^{occup} \varphi_{\alpha i}^*(\vec{r}')\,\varphi_{\alpha i}(\vec{r})$

= KOHN-SHAM ONE-PARTICLE DENSITY MATRIX

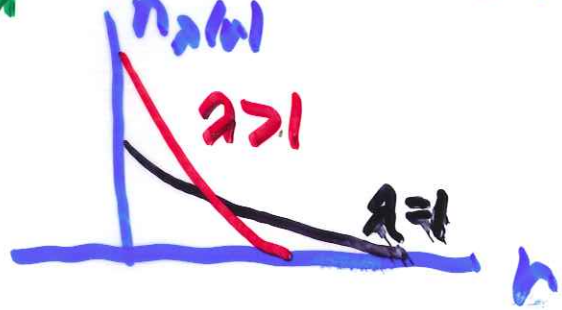
EXACT CONSTRAINTS: WE KNOW MANY EXACT CONSTRAINTS ON THE HOLE (SUCH AS THE SUM RULE) OR ON THE X_C ENERGY.

EX: UNIFORM DENSITY SCALING OF $E_x[n]$

LEVY + PERDEW

FOR ANY POSITIVE SCALE PARAMETER λ,
DEFINE A SCALED DENSITY

$$n_\lambda(\vec{r}) = \lambda^3 n(\lambda \vec{r})$$



WHEN $n(\vec{r}) \to n_\lambda(\vec{r})$,

$\psi_\alpha(\vec{r}) \to \lambda^{3/2} \psi_\alpha(\lambda \vec{r})$,

SO

$$E_x[n_\lambda] = \lambda E_x[n]$$

HIGH-DENSITY LIMIT: $\lambda \to \infty$

$E_c[n_\lambda] \to$ CONSTANT (NOKS DECREASES)

E_x DOMINATES E_c

MANY OTHER EXACT CONSTRAINTS ON $n_{xc}(\mathbf{r},\mathbf{r}')$ OR $E_{xc}[n]$ HAVE BEEN DERIVED. THESE CONSTRAINTS HAVE BEEN USED TO CONSTRUCT APPROXIMATIONS TO $E_{xc}[n]$, WITHOUT (OR WITH) FITTING TO DATA.

FULLY NONEMPIRICAL

LOCAL DENSITY APPROXIMATION

PBE GENERALIZED GRADIENT APPROX.

TPSS AND REVTPSS META-GGA.

WE CAN CONSTRUCT THE EXACT $E_x[n]$ FROM KOHN-SHAM ORBITALS (AS IN OEP), BUT BONDS ARE DESCRIBED BETTER WHEN WE MAKE THE SAME LOCAL OR SEMI-LOCAL APPROXIMATION FOR E_x AND FOR E_c. THAT IS BECAUSE $n_{xc}^2(\vec{r},\vec{r}')$ IS TYPICALLY DEEPER, MORE SHORT-RANGED IN $|\vec{r}'-\vec{r}|$, AND THUS MORE SEMI-LOCAL THAN IS $n_x(\vec{r},\vec{r}')$. AS A RESULT, THE ERRORS OF SEMI-LOCAL EXCHANGE TEND TO CANCEL THOSE OF SEMI-LOCAL CORRELATION, FOR MANY SYSTEMS NEAR EQUILIBRIUM.

SIMPLEST DENSITY FUNCTIONAL: LOCAL DENSITY APPROXIMATION

$$E_{xc}^{LDA}[n] = \int d^3r\, n(\vec{r})\, \varepsilon_{xc}^{unif}(n(\vec{r}))$$

$\varepsilon_{xc}^{unif}(n)$ = xc ENERGY PER ELECTRON FOR AN ELECTRON GAS OF UNIFORM DENSITY n.

EXACT FOR A UNIFORM DENSITY.
CORRECTIONS FOR A SLOWLY-VARYING DENSITY $\sim |\nabla n|^2$.

$n_{xc}^{LDA}(\vec{r}, \vec{r}') = n_{xc}^{unif}(n(\vec{r}); |\vec{r}-\vec{r}'|)$

SATISFIES SUM RULE AND SEVERAL OTHER EXACT CONSTRAINTS, INCLUDING SCALING FOR X.
(WHY IT "WORKS".)

LDA WAS THE ORIGINAL DENSITY FUNCTIONAL APPROX. (KOHN-SHAM).

IT PROVED TO BE SURPRISINGLY ACCURATE IN SOLID STATE PHYSICS, WHERE IT IS STILL SOMETIMES USED TODAY.

MORE ACCURATE APPROXIMATIONS HAD TO BE DEVELOPED FOR ATOMS & MOLECULES (WHICH ARE LESS LIKE THE UNIFORM ELECTRON GAS).

WIDELY USED IN CHEMISTRY NOW:

GENERALIZED GRADIENT APPROX. (GGA)

META-GGA

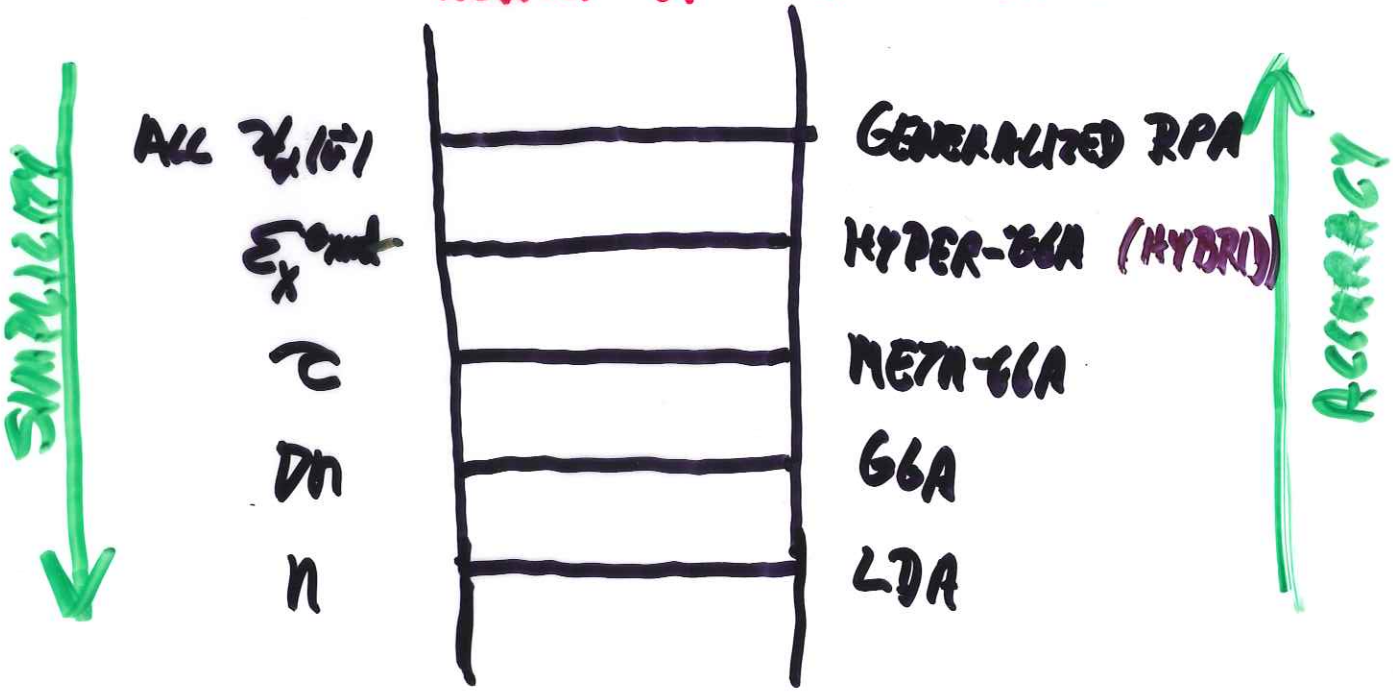
GLOBAL HYBRIDS OF GGA OR META-GGA WITH EXACT EXCHANGE

JACOB'S LADDER OF DENSITY FUNCTIONAL APPROXIMATIONS

$$E_{xc} = \int d^3r \, f(n, \nabla n, \tau, \ldots)$$

$$\tau(\vec{r}) = \sum_{\alpha}^{\text{occ}} \tfrac{1}{2} |\nabla \psi_\alpha|^2 = \text{POSITIVE KE DENSITY}$$

HEAVEN OF CHEMICAL ACCURACY



HARTREE WORLD

ADDING MORE INGREDIENTS PERMITS US TO SATISFY MORE EXACT CONSTRAINTS, OR TO FIT DATA BETTER.

SEMI-LOCAL APPROXIMATIONS, IN WHICH THE XC ENERGY DENSITY $f(\underset{\sim}{r})$ IS CONSTRUCTED FROM THE DENSITY OR OCCUPIED ORBITALS IN AN INFINITESIMAL NEIGHBORHOOD OF POSITION $\underset{\sim}{r}$:

LDA, GGA, META-GGA

ALL OF COMPARABLE COST.

ALL HAVE NONEMPIRICAL CONSTRUCTIONS.

META-GGA IS ACCURATE FOR EQUILIBRIUM PROPERTIES, USUALLY, BUT NOT FOR STRETCHED BONDS.

FULLY NONLOCAL APPROXIMATIONS:

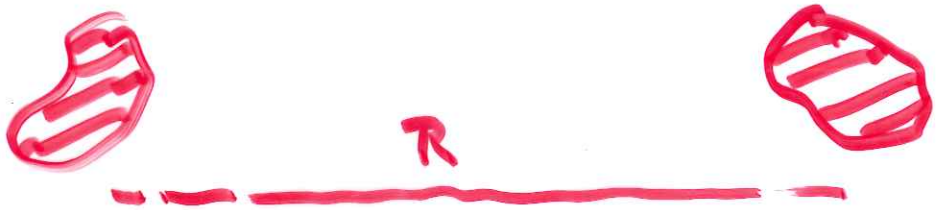
HYPER-GGA

GENERALIZED RPA

MORE EXPENSIVE THAN SEMI-LOCAL APPROXIMATIONS.

NEEDED TO DESCRIBE STRETCHED BONDS. POTENTIALLY "SELF-INTERACTION-FREE."

FULLY NONLOCAL APPROXIMATIONS ARE ALSO NEEDED TO DESCRIBE THE LONG-RANGE VAN DER WAALS INTERACTION $-\frac{C_6}{R^6}$



TYPICAL RELATIVE ERRORS FOR MOLECULES

EQUILIBRIUM

BOND LENGTHS AT EQUILIBRIUM :

LESS THAN	1%

ATOMIZATION ENERGIES :

LDA	15%
GGA	3%
META-GGA	1%
HYPER-GGA	1%

STRETCHED BONDS

ENERGY BARRIERS TO CHEMICAL REACTIONS

LDA	100%
GGA	80%
META-GGA	60%
HYPER-GGA	30%

GENERALIZED GRADIENT APPROX. (GGA)

$$E_{xc}^{GGA}[n] = \int d^3r \, e_{xc}^{GGA}(n, |\nabla n|)$$

FOR PROPER SCALING,

$$E_x^{GGA}[n] = \int d^3r \, n(\vec{r}) \, \varepsilon_x^{unif}(\vec{r}) \, F_x(s)$$

$$s = \frac{|\nabla n|}{2 (3\pi^2)^{1/3} n^{4/3}} = \text{reduced density gradient}$$

UNLIKE LSDA, THE PBE GGA CORRELATION ENERGY SCALES PROPERLY TO A CONSTANT IN THE HIGH-DENSITY LIMIT.

BIFURCATION AT THE GGA LEVEL:

PBE (1996) IS BETTER FOR ATOMS + MOLECULES.

PBEsol (2008) IS BETTER FOR SOLIDS + SURFACES.

THE GGA FORM IS TOO SIMPLE.

PBE WAS DERIVED FROM XC HOLE CONSTRAINTS, & PBEsol WAS CONSTRUCTED TO RECOVER THE CORRECT SECOND-ORDER GRADIENT EXPANSION FOR EXCHANGE.

META-GGA

$$E_{xc}^{MGGA}[n] = \int d^3r\, e_{xc}^{MGGA}(n, \nabla n, \tau)$$

THE TPSS AND REVTPSS META-GGA'S ARE CONSTRUCTED TO SATISFY MANY EXACT CONSTRAINTS ON $E_{xc}[n]$

REVTPSS SEEMS TO GIVE A GOOD SIMULTANEOUS DESCRIPTION OF MANY ATOMS, MOLECULES, SOLIDS, & SURFACES.

REVTPSS IS AVAILABLE NOW IN VASP + BAND.

HOW A META-GGA CAN DISTINGUISH BETWEEN ATOMS & MOLECULES ON THE ONE HAND, & SOLIDS (ESPECIALLY METALS) ON THE OTHER:

$$\alpha \equiv \frac{\tau - \tau_W}{\tau^{unif}}$$

WHERE $\tau_W = \frac{|\nabla n|^2}{8n}$, $\tau^{unif} = \frac{3}{10}(3\pi^2)^{2/3} n^{5/3}$

ATOMS + MOLECULES HAVE REGIONS WHERE $\alpha \simeq 0$.

SOLID METALS HAVE REGIONS WHERE $\alpha \simeq 1$.

24/11 a

HYPER-GGA (LOCAL HYBRID)

$$E_{xc}^{\text{HYPER}}[n] = \int d^3r \left[a(\vec{r})\, e_x^{\text{EXACT}}(\vec{r}) + \{1 - a(\vec{r})\}\, e_x^{\text{MGGA}}(\vec{r}) \right] + E_c^{\text{MGGA}}[n]$$

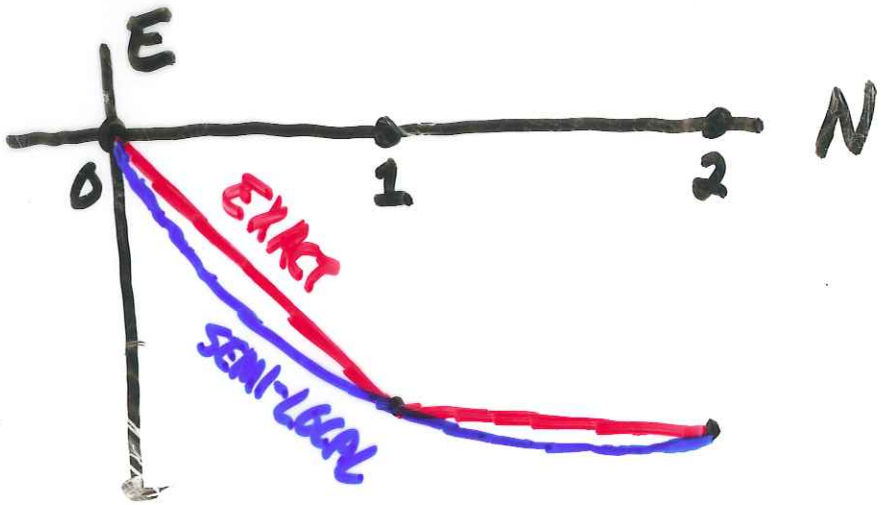
$a(\vec{r})$ = LOCAL MIXING FRACTION OF EXACT EXCHANGE (A CONSTANT ~0.1 IN THE GLOBAL HYBRID).

JUSTIFIED BY BECKE'S ARGUMENT FROM THE COUPLING-CONSTANT INTEGRAL.

WITH THE RIGHT CHOICE OF $a(\vec{r})$, NEARLY ALL KNOWN EXACT CONSTRAINTS CAN BE SATISFIED.

STRETCHED-BOND OR SELF-INTERACTION PROBLEM

NON-INTEGER ELECTRON NUMBER N CAN ARISE AS THE AVERAGE OF FLUCTUATING ELECTRON NUMBER IN AN OPEN SYSTEM. SEMI-LOCAL APPROX'S ASSIGN TOO LOW AN ENERGY IN THIS CASE.



EXACT "ENSEMBLE" THEORY: PERDEW, PARR, LEVY + BALDUZ 1982

THE SEMI-LOCAL XC HOLE IS LOCALIZED IN THE OPEN SYSTEM. THE EXACT HOLE IS NOT.

SIMILAR STRAIGHT-LINE BEHAVIOR OF THE EXACT FUNCTIONAL FOR FRACTIONAL SPIN HAS BEEN DERIVED BY WEITAO YANG & COLLABORATORS.

CONSEQUENCES FOR EXACT THEORY:

(1) THE ORBITAL ENERGY OF THE HIGHEST OCCUPIED OR PARTLY-OCCUPIED ORBITAL IS

$$\varepsilon^{HO} = \frac{dE}{dN} = \mu = -I,$$

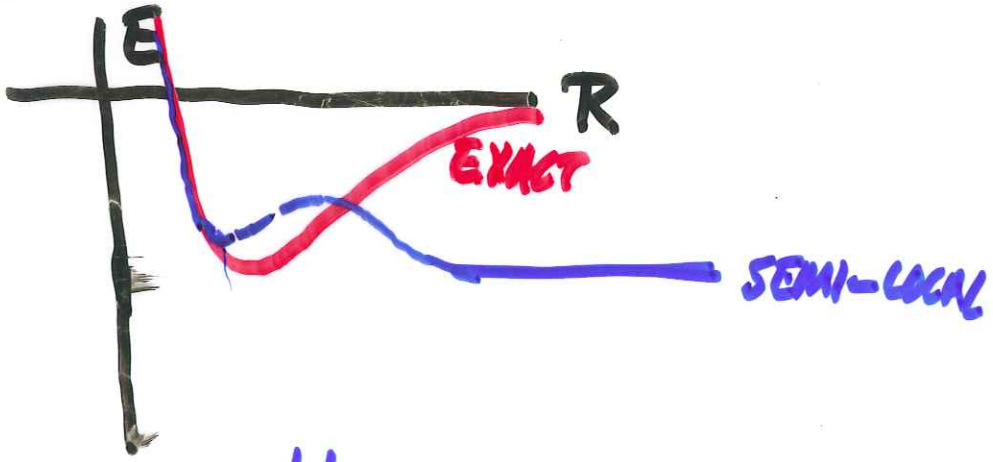
MINUS THE IONIZATION ENERGY.

(2) THE EXACT XC POTENTIAL JUMPS UP BY A FINITE CONSTANT AS THE ELECTRON NUMBER CROSSES AN INTEGER. THE GAP IN THE EXACT KOHN-SHAM BANDSTRUCTURE AT FIXED N IS THUS LESS THAN THE EXPERIMENTAL GAP.

CONSEQUENCES FOR SEMI-LOCAL APPROX'S

(1) DIATOMIC MOLECULES AB OFTEN DISSOCIATE INCORRECTLY TO FRACTIONALLY-CHARGED FRAGMENTS $A^{+\delta} \ldots B^{-\delta}$.

(2) RADICAL MOLECULES LIKE H_2^{+1} OR Ne_2^{+1} HAVE INCORRECT BINDING ENERGY CURVES



NOTE THAT H_2^{+1} IS A ONE-ELECTRON SYSTEM, FOR WHICH SEMI-LOCAL APPROX'S ARE NOT EXACT. IT DISSOCIATES TO $H^{+0.5} \ldots H^{+0.5}$

(3) ENERGY BARRIERS TO CHEMICAL REACTIONS ARE TOO LOW, BECAUSE THE TRANSITION STATES HAVE STRETCHED BONDS CONNECTING FRACTIONALLY-CHARGED FRAGMENTS.

(4) TRANSITION-METAL OXIDES HAVE INCORRECT BOND LENGTHS & MAGNETIC MOMENTS, BECAUSE THE NUMBER OF d ELECTRONS CAN FLUCTUATE.

FOR THESE OUTSTANDING PROBLEMS OF DFT, FULL NONLOCALITY IS NEEDED. FULLY NONLOCAL FUNCTIONALS CAN HAVE FULL EXACT EXCHANGE, AND BE EXACT FOR ALL ONE-ELECTRON DENSITIES.

GROUND-STATE DFT

$$n(\underline{r}) \rightarrow v(\underline{r})$$

TIME-DEPENDENT DFT

$$n(\underline{r},t) \text{ AND } \Psi_{\text{INITIAL}}$$

$$\rightarrow v(\underline{r},t)$$

COMMON ADIABATIC APPROX.

$$v_{xc}(\underline{r},t) = v_{xc}^{GS}([n(\underline{r},t)];\underline{r})$$

EX: A MOLECULE IN A STRONG OR WEAK TIME-DEPENDENT LASER FIELD.

TIME-DEPENDENT KS EQN

$$\left[-\tfrac{1}{2}\nabla^2 + v_s(\underline{r},t)\right]\psi_k(\underline{r},t) = i\hbar\frac{\partial}{\partial t}\psi_k(\underline{r},t)$$

TIME-DEPENDENT LINEAR RESPONSE

LET A SYSTEM INITIALLY IN ITS GROUND-STATE BE PERTURBED BY A WEAK TIME-DEPENDENT EXTERNAL POTENTIAL $\delta v(\underline{r},t)$.

DENSITY RESPONSE AT FREQUENCY ω:

$$\delta n(\underline{r},\omega) = \int d^3r' \chi(\underline{r},\underline{r}',\omega)\,\delta v(\underline{r}',\omega)$$

THE FREQUENCIES ω AT WHICH χ HAS A POLE ARE THE EXCITATION ENERGIES OF THE SYSTEM. (RESONANCE OR NATURAL FREQUENCIES).

NOW WIDELY USED TO CALCULATE EXCITATION ENERGIES OF MOLECULES.

COMMONLY-USED UNITS.

START FROM cgs UNITS (cm, gm, sec), IN WHICH

$$u = \frac{g_1 g_2}{|\vec{r}_1 - \vec{r}_2|}.$$

SWITCH TO ATOMIC UNITS, IN WHICH

$$\hbar = m = e^2 = 1.$$

ATOMIC UNIT OF DISTANCE

$$a_0 = 1 \text{ bohr} = \frac{\hbar^2}{me^2} = 0.5292 \text{ Å}$$

ATOMIC UNIT OF ENERGY

$$1 \text{ hartree} = \frac{e^2}{a_0} = 27.21 \text{ eV}$$

$= 627.5\ kcal/mol = 219475\ cm^{-1}$

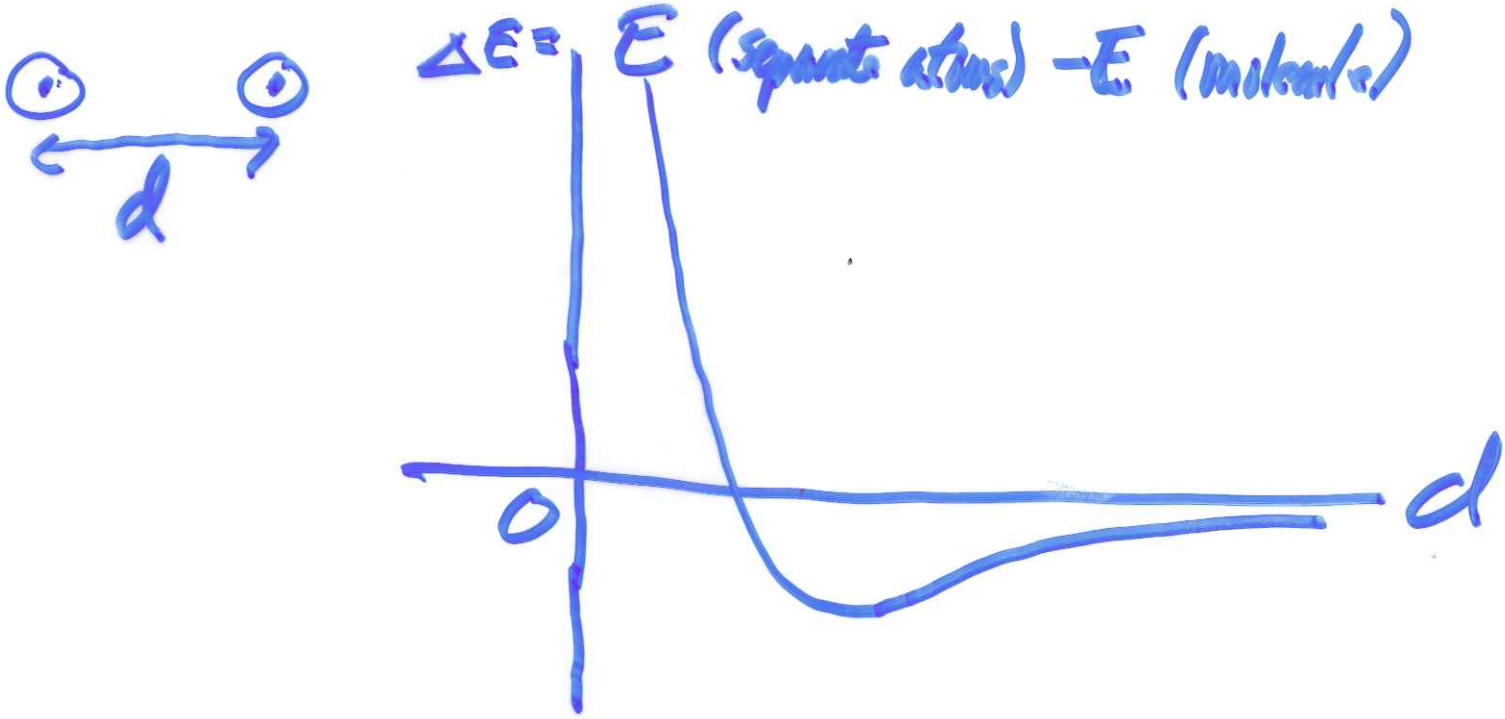
STANDARD GROUND-STATE PROPERTIES

FIRST IONIZATION ENERGY

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

WHERE N = ELECTRON NUMBER AT NEUTRALITY.

BINDING ENERGY CURVE OF A DIATOMIC MOLECULE



AT THE MINIMUM,

ΔE = AE = ATOMIZATION ENERGY

d = EQUILIBRIUM BOND LENGTH.

E

IN A FIRST APPROXIMATION, E IS COMPUTED FOR STATIC NUCLEI.

IN A BETTER APPROXIMATION, E INCLUDES THE ZERO-POINT VIBRATIONAL ENERGY OF THE MOLECULE,

$$\frac{\hbar\omega}{2}$$

THE EQUILIBRIUM BOND LENGTH FOR STATIC NUCLEI CAN ALSO BE COMPUTED BY ZEROING OUT THE NET ELECTROSTATIC FORCE ON EACH NUCLEUS (HELLMANN-FEYNMAN THEOREM).

WHEN THERE ARE MANY NUCLEI, THIS IS THE MOST EFFICIENT WAY TO FIND THE EQUILIBRIUM GEOMETRY.

$$-\frac{\partial}{\partial R_\beta}\langle \hat{H} \rangle = -\left\langle \frac{\partial \hat{H}}{\partial R_\beta} \right\rangle$$

(F)

EXPERIMENTAL VALUES FOR NITROGEN, FROM THE COMPUTATIONAL CHEMISTRY COMPARISON AND BENCHMARK DATABASE

cccbdb.nist.gov

$I(N) = 14.5\ eV$

$AE(N_2) = AE(STATIC) - \frac{\omega_e}{2}$

$= 225.1\ kcal/mol$

EQUILIBRIUM $d = 1.098\ \text{Å}$

COMPUTE THESE WITH GAUSSIAN

PBE GGA

6-311++G(3df,3pd) BASIS SET

ULTRAFINE GRID