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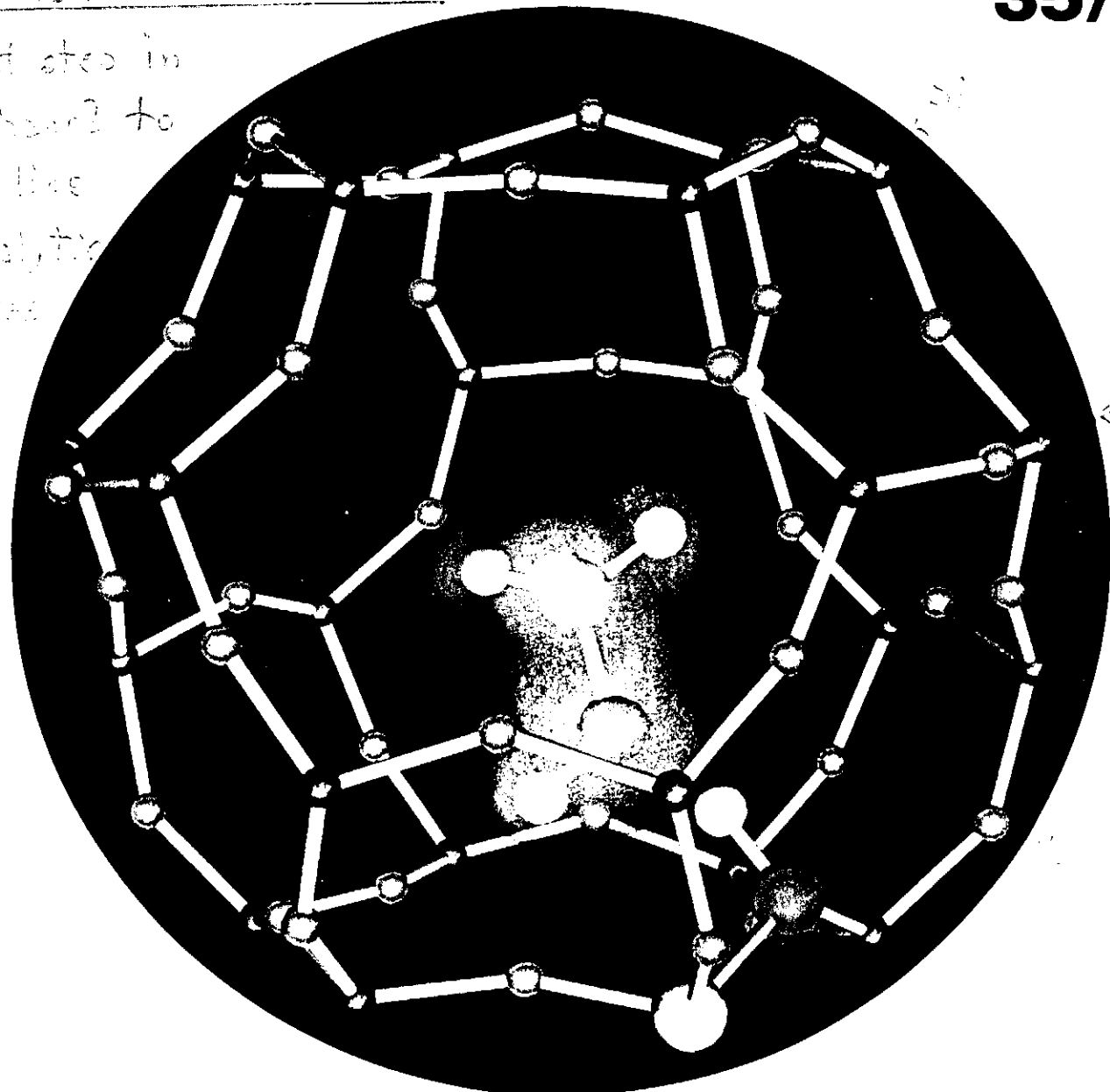
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Methanol in a zeolite

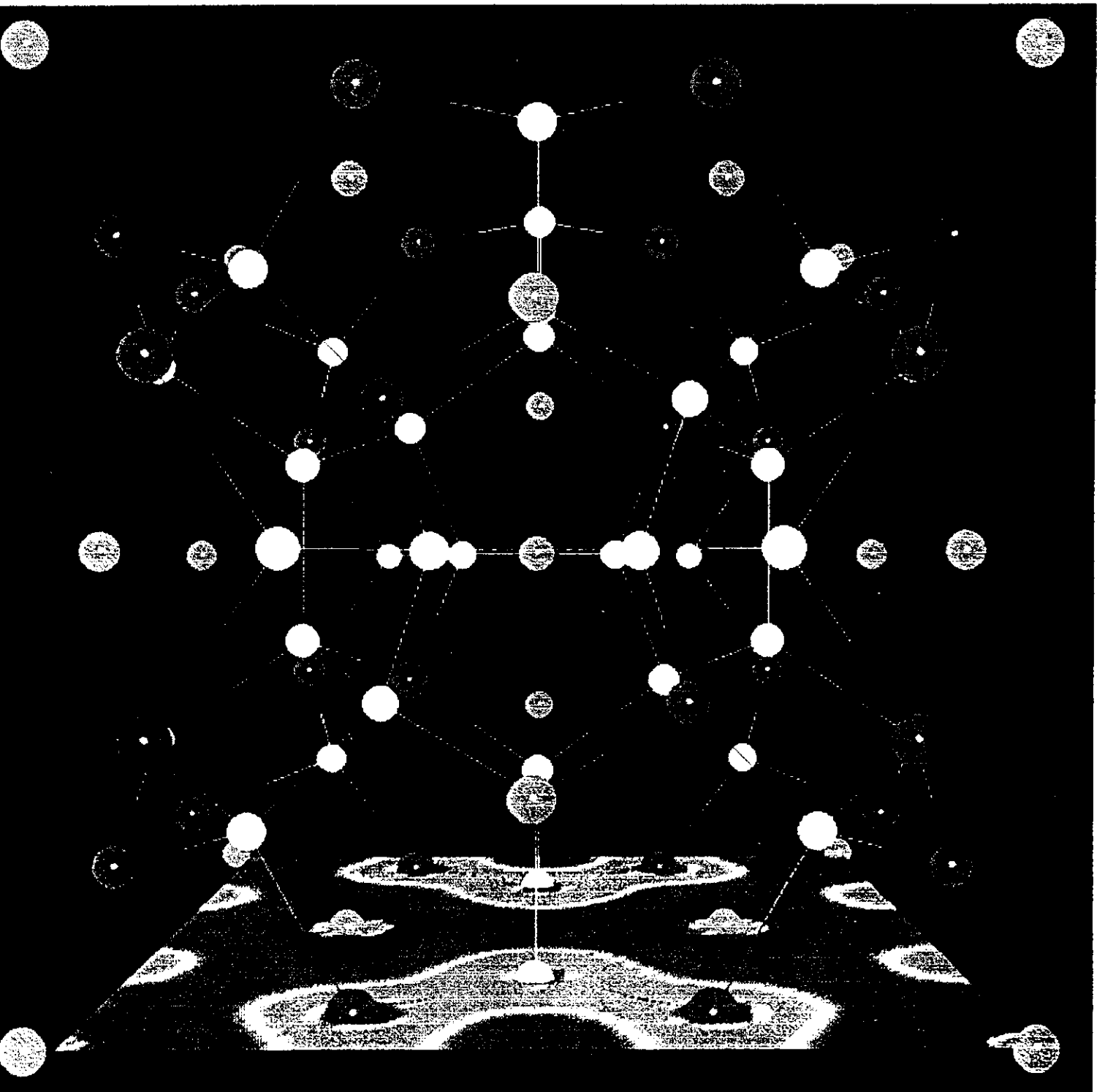
first step in
methanol to
gasoline
catalytic
process



Reviews: Electronegativity and Molecular Properties · Al³⁺ and Ga³⁺ Compounds
Highlights: Proteins that Bind Vitamin B₁₂ · Cyclic Eneidyne

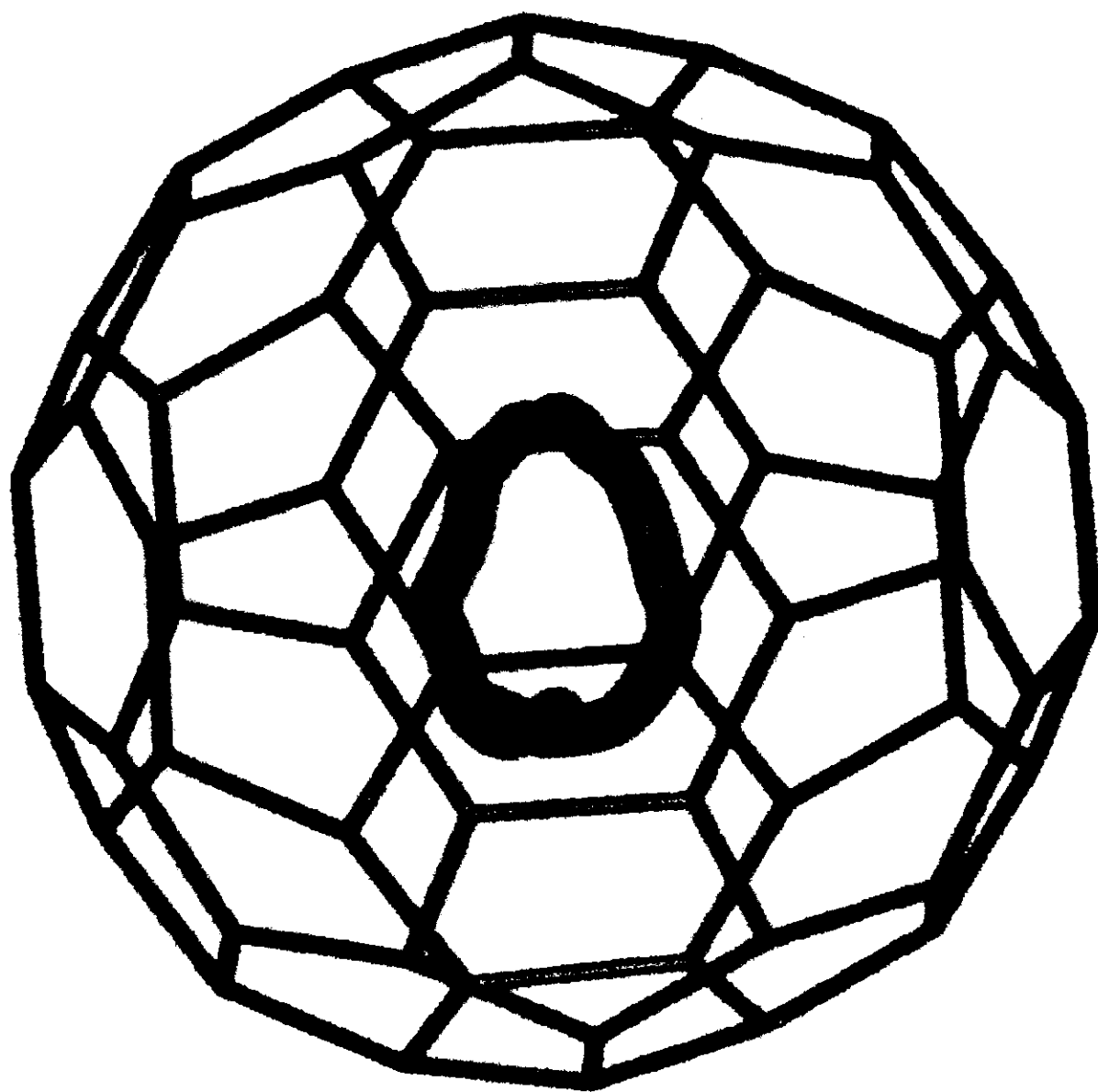
Angew Chem 35 117 (1996)

Work of H. M. ...
(in progress)



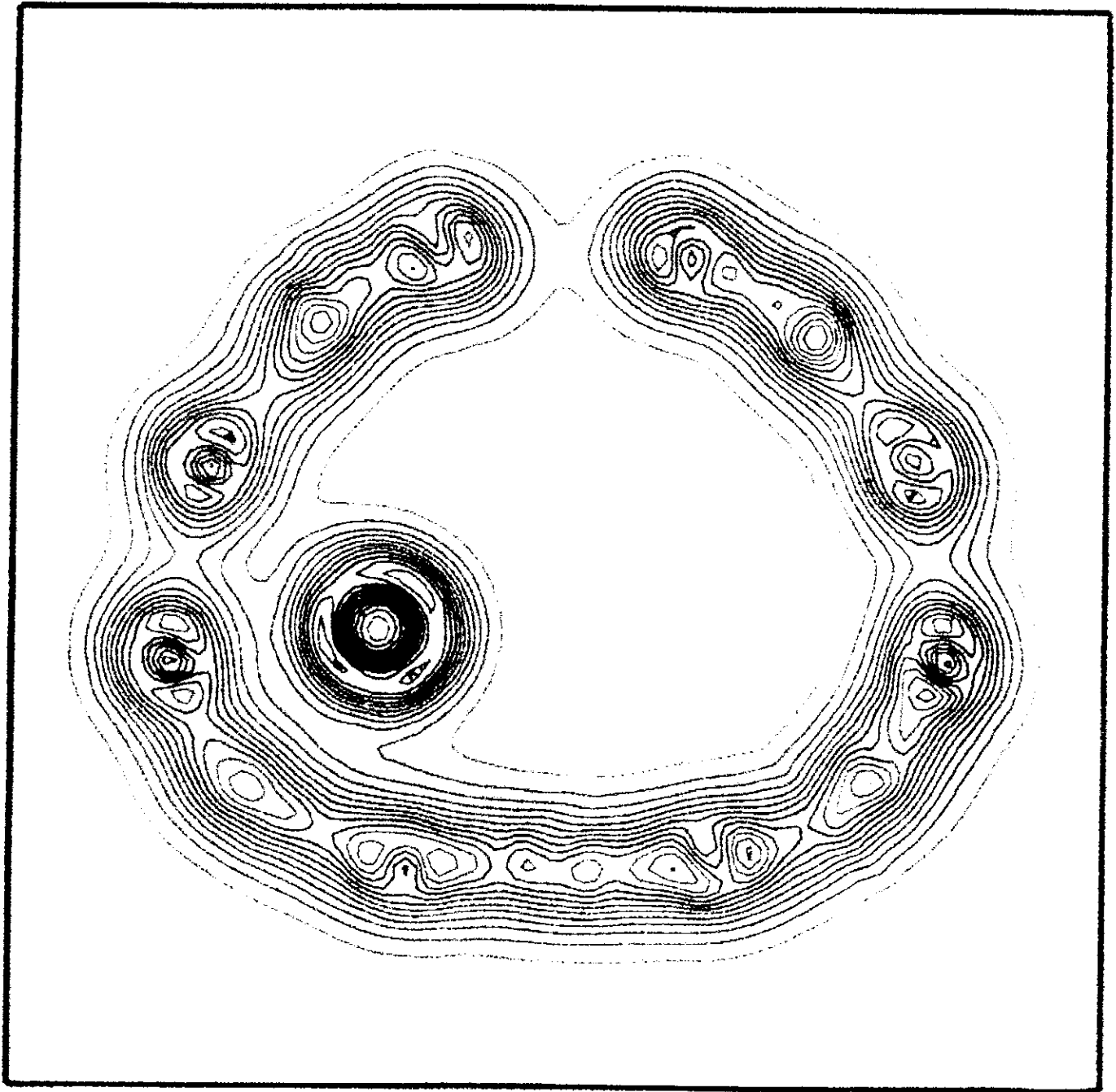
The geometric and distance structure of the
cluster $Sr_2Ca_{16}Ge_{30}$. Metal or insulator?

La @ C₆₀



Group of W. Andreoni

La @ C₈₂



Group of W. Andreoni

Electronic Structure of Matter -

Wave Functions and Density Functionals.

1. Introduction - History
2. Schrodinger Wave Functions - Few vs. Many Electrons
3. Density Functionals - Theoretical Considerations
and Applications
4. Concluding Remarks

Introduction

History

Two beginnings in late 1920's:

1. Schrodinger: Wave functions, $\Psi(r_1, r_2, \dots, r_N)$.

Complete, powerful, in principle arbitrarily accurate

Dirac's dictum about the "end of chemistry".

2. Thomas-Fermi: Density distribution $n(r)$.

Heuristic, simple, crude, major problems near nuclei and edges.

For next ~35 years most progress based on 1: Hylleraas

Hartree, Heitler-London, Bloch-Mulliken, James-

Coolidge, Pauling, Hartree-Fock + CI, Pople-Computer.

Also several corrections applied to 2: Exchange, correlation, grad $n(r)$. Still crude, no molecular binding; no firm basis \rightarrow computers little use.

2. Schrodinger Wave Functions - Few vs. Many Electrons

The Schrodinger Eqn.

$$\left\{ -\frac{\hbar^2}{2m} \sum_j \nabla_j^2 - \sum_{j \neq \alpha} \frac{Z_\alpha e^2}{|r_j - R_\alpha|} + \sum_{j \neq j'} \frac{1}{|r_j - r_{j'}|} - E \right\} \Psi = 0$$

Born-Oppenheimer: R_α fixed

$\Psi = \Psi(r_1, r_2, \dots, r_N)$ spin suppressed

$P_{jj'} \Psi = -\Psi$. Pauli principle

$E = E(R_1, \dots, R_M)$

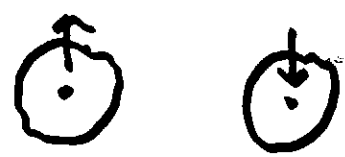
$n(r) = n(r; R_1, \dots, R_M)$ etc.

Few Electrons - The H₂ Molecule.

Heitler London - Valence Bond Orbitals.

$$\Psi = \underset{\substack{\nearrow \\ \text{norm.}}}{N} \left[\varphi_H(r_1 - R_1) \varphi_H(r_2 - R_2) + \varphi_H(r_2 - R_1) \varphi_H(r_1 - R_2) \right] \chi_0$$

↑
Singlet



$$E(R_1, R_2) = (\Psi, H\Psi)$$

Good for $R_{12} = 0$ and $R_{12} = \infty$

	HL	Expt
R	0.87 Å	0.74 Å
B	3.14 eV	4.75 eV

Bloch-Mullikan Molecular Orbitals

$$\Psi = [\varphi_{BM}(r_1) \varphi_{BM}(r_2)] \chi_0$$



$$\varphi_{BM}(r_i) = N' [\varphi_H(r_i - R_1) + \varphi_H(r_i - R_2)]$$

Good for $R_{12} = 0$, bad for $R_{12} \rightarrow \infty$

R	0.76 Å
B	2.65 eV

Hartree - Fock

Replace $\psi_{BM}(r) \rightarrow \psi_{sym}(r)$ genl sym. fn

Determinantal Wave Fn:

$$\Psi = \text{Det} (\psi_{sym}(r_1) \alpha(1) \psi_{sym}(r_2) \beta(2))$$

$$E = (\Psi, H \Psi)$$

Minimization with respect to $\psi_{sym}(r)$ leads to non-local HF equation.

R	≠	0.74 Å
B		3.63 eV

James and Coolidge

Variational 2-electron ^{trial} wave function

$$\Psi = \tilde{\Psi}_{\text{sym}}(r_1, r_2) \chi_0$$

No. of variables = $3 \times 2 - 1 = 5$

Brute force: Need ≈ 10 trial function/variable
 $\approx 10^5$!!

Intelligent choice: 3 functions/variable = $3^5 = 250$
 OK

Extended J-C variational calcn with 50 terms gives "perfect" agreement with expt

* "perfect": $\delta R \ll 0.01 \text{ \AA}$, $\delta B \ll 0.01 \text{ eV}$

For sufficiently small molecules WF methods give excellent results

Many Electrons - Fighting an Exponential Wall

N electrons, ν functions/variable

Take max. total basis, \mathcal{N}_{\max}

Call N_{\max} the max. manageable no. of elec.

$$\nu^{3N_{\max}} = \mathcal{N}_{\max}$$

$$N_{\max} = \frac{1}{3} (\log_{10} \mathcal{N}_{\max} / \log_{10} \nu)$$

Example: $\mathcal{N}_{\max} = 10^9$

$$\nu = 3$$

$$N_{\max} \approx 7 \text{ els } (!)$$

Need chemical ingenuity to vastly reduce required basis from our estimate, $\nu^{3N_{\max}}$.

But exponential dependence of \mathcal{N}_{\max} on N_{\max} for many electron - many atom systems remains.

Traditional w.f. methods are limited to small N

Some Metaphysical (-chemical) Thoughts

(Related to the "Van Vleck Catastrophe")

A provocative statement:

In general the many-electron wave function for $N \gg N_0$ ($\approx 10^3$) is not a legitimate scientific concept.

Figure of merit for approximate Ψ_{app} :

$$\gamma \equiv (\bar{\Psi}, \Psi_{\text{app}}) \equiv 1 - \alpha$$

e.g. require $\alpha \leq 0.1$, 90% overlap.

Argument 1. For $N \gg N_0$ a "good" Ψ_{app} cannot be calculated, in general.

Ex: Non-interacting typical atoms

$$\underline{\Psi}(r_1, \dots, r_N) = A(\psi_1(r_1) \dots \psi_N(r_N))$$

$$\bar{\Psi}_{\text{app}}(r_1, \dots, r_N) = A(\psi'_1(r_1) \dots \psi'_N(r_N))$$

Suppose all ψ'_j are accurately calculated with

$$\gamma_j \equiv (\Psi_j, \psi'_j) = 1 - \alpha_j \quad \alpha_j \ll 1$$

Then, for many-electron Ψ

$$\gamma \equiv (\Psi, \Psi_{\text{app}}) = \prod_j \gamma_j$$

$$\log \gamma = \sum_j \log \gamma_j = + \sum_j \log (1 - \alpha_j) = - \sum_j \alpha_j = -N_0 \langle \alpha_j \rangle$$

$$\gamma = e^{-N_0 \langle \alpha_j \rangle}$$

Thus if we require $\gamma > 0.9$,

$$N_0 \langle \alpha_j \rangle \leq 0.1 \quad \langle \alpha_j \rangle \leq 10^{-4} \quad \text{impossible for typical atom.}$$

For strongly interacting atoms, situation much worse.

Argument 2. $\Psi(r_1, r_2, \dots, r_N)$ cannot be recorded in general.

For N_0 strongly correlated atoms need

$$10^2 (> 10^2) \text{ bits/atom, or a total of } (10^2)^{N_0} = 10^{2000} \text{ bits.}$$

Unfeasible

In general, for $N \geq N_0 (\approx 10^3)$, even the best approximate many-electron Ψ_{app} have a negligible overlap with the exact Ψ .

NEVERTHELESS

Even some very "bad" Ψ_{app} can be used successfully to calculate quantities which depend only on a few variables near each other such as $n(r)$, $g(r_1, r_2)$ etc., and - from them - total energies E , forces on nuclei, F_L , etc.

Concept of "neersightedness" (W.K., PRL 76, 3168
1996)

This needs deeper analysis.

Density Functional Theory avoids use of many-electron functions $\Psi(r_1, \dots, r_N)$

Introduction to DFT

Consider following systems: M fixed nuclei (R_i, Z_i) and N electrons (r_i) in their ground state.

Schroedinger equation:

$$\left\{ -\frac{\hbar^2}{2m} \sum_j \nabla_j^2 + \sum_j v(r_j) + \frac{1}{2} \sum_{\substack{j, j'=1 \\ j \neq j'}}^N \frac{e^2}{|r_j - r_{j'}|} - E \right\} \Psi(r_1, \dots, r_N) = 0, \quad (1)$$

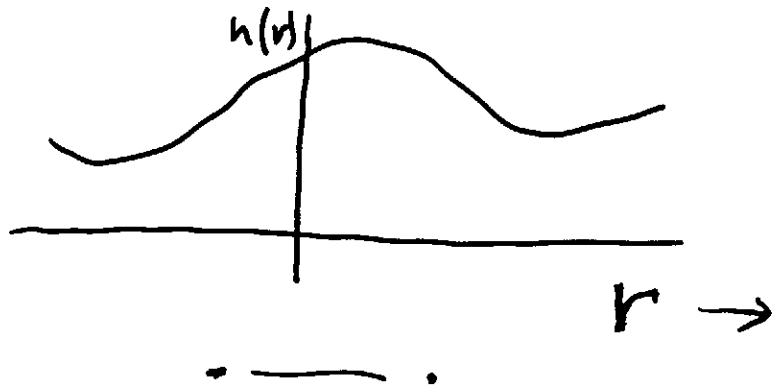
where

$$v(r_j) = - \sum_{i=1}^M \frac{Z_i e^2}{|r_j - R_i|}. \quad (2)$$

Questions: For given (R_i, Z_i) what are E , $n(r)$ (density distribution)?

Traditional methods for solving S.E. (1) become unmanageable for $N \gtrsim N_0$, where typically $N_0 \sim 10$ or so.

Density functional theory (DFT) reformulates the problem of solving the 3N-dimensional Schr. Eqn. (1) for $\Psi(r_1, \dots, r_N)$ in terms of a problem involving the electron 3-dimensional density, $n(r)$, for any N .



1. BASIC LEMMA OF HK

Statement:

If a potential $v(r)$ leads to the ground state density $n(r)$, and $v'(r)$ also leads to $n(r)$, then

$$v'(r) = v(r) + C, \quad (3)$$

i.e. $n(r) \rightarrow v(r)$ "uniquely" (to within an uninteresting additive constant)

Proof (for non-degenerate ground state):

$$v(r) \rightarrow H, n(r), \Psi, E$$

$$v'(r) \rightarrow H', n'(r) (= n(r)), \Psi', E'$$

Assume $v'(r) \neq v(r) + C$ (reductio ad absurdum) (*)

Then $\Psi' \neq \Psi$.

$$E = (\Psi, H \Psi) < (\Psi', H \Psi') = (\Psi', H' \Psi') + \int (v(r) - v'(r)) n'(r) dr$$

↑
Rayleigh-Ritz

$$= E' + \int (v(r) - v'(r)) n'(r) dr \quad (I)$$

Interchange primed and unprimed quantities:

$$E' < E + \int (v'(r) - v(r)) n(r) dr$$

$$= E + \int (v'(r) - v(r)) n'(r) dr. \quad (I')$$

Add the 2 inequalities I and I':

$$E + E' < E + E'$$

Hence (*) wrong.

$$\therefore v'(r) = v(r) + C.$$

Observations:

Since $n(r)$ ^{of ground state} determines $v(r)$, it determines H

and hence, in principle, all quantities derivable from H , e.g.

Spectrum: E_0, E_1, E_2, \dots

N-body wave-functions: $\Psi_0(r_1, r_2, \dots, r_N)$
 $\Psi_1(r_1, r_2, \dots, r_N)$

.....

Correlation functions: $g_2(r_1, r_2), \dots$

Etcetera.

2. ENERGY VARIATIONAL PRINCIPLE OF HK.

Preliminary: Universal Functional.

$$E = (\bar{\Psi}, H \bar{\Psi}) = (\bar{\Psi}, \left(\underset{\substack{\uparrow \\ \text{kinetic}}}{T} + \underset{\substack{\uparrow \\ \text{ext.} \\ \text{potential}}}{V} + \underset{\substack{\uparrow \\ \text{interaction}}}{U} \right) \bar{\Psi})$$

$$(\bar{\Psi}, V \bar{\Psi}) = \int v(r) n(r) dr$$

$$(\bar{\Psi}, (T+U) \bar{\Psi}) \equiv F[n(r)], \quad \text{universal functional (4) of } n(r) \text{ (which are ground state densities - VR problem)}$$

The Variational Principle.

Define energy functional of trial density, $n'(r)$:

$$E_{v(r)}[n'(r)] \equiv \int v(r) n'(r) dr + F[n'(r)] \quad (5)$$

↑
given

Theorem:

$$E_{v(r)}[n'(r)] \geq E_{v(r)}[n(r)] = E \quad (6)$$

↑
correct $n(r)$ for given $v(r)$

Proof based on Rayleigh-Ritz varl. principle.

Further
Observations:

1. Contrast to Rayleigh-Ritz variational principle

$$E_{V(r)}[\Psi'] \equiv (\Psi', H\Psi') \geq (\Psi, H\Psi) = E$$

↑ trial function

$\Psi'(r_1, r_2, \dots, r_N)$ depends on $3N$ variables

$n'(r)$ depends on 3 variables

However HK variational principle requires
adequate knowledge of $F[n'(r)]$

(See below)

2. Relation to Thomas Fermi approximation.

TF is obtained by approximating

$$F[n(r)] \sim \gamma \int n^{5/3}(r) dr + \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|} dr dr'$$

↑
kinetic

↑
interaction.

$$\gamma = \frac{3}{5} \frac{\hbar^2}{2m} (3\pi^2)^{2/3}$$

From

$$K.E. = \int \frac{3}{5} k_F^2 n(r) dr \quad k_F(r) = (3\pi^2)^{1/3} n(r)^{1/3}$$

3. EXACT VERSION OF HARTREE EQUATIONS (KS)

Derivable from "exact" HK variational principles as Euler-Lagrange equations.

Preliminary: Defn. of Exchange Correlation Energy, E_{xc}

$$F[n(r)] \equiv T_s[n(r)] + \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|} + E_{xc}[n(r)]$$

↑
Defn of E_{xc}

$T_s[n(r)] \equiv$ kin. energy of non-interacting electrons with ground state density $n(r)$

KS Equations.

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + v(r) + \int \frac{n(r')}{|r-r'|} dr' + \underbrace{v_{xc}(r)}_{\text{new}} - \epsilon_j \right\} \psi_j = 0 \quad (7)$$

$j = 1, \dots, N$

$$v_{xc}(r) \equiv \frac{\delta E_{xc}[n(r)]}{\delta n(r)} \quad (\text{exch.-correl. potential}) \quad (8)$$

$$n(r) = \sum_1^N |\psi_j(r)|^2 \quad (9)$$

Observation: If exact $v_{xc}(r)$ is used, these Hartree-like equations give exact $n(r)$ and E including all many-body effects.

$$E = \sum \epsilon_j - \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|} dr dr' + E_{xc}[n] - \int v_{xc}(r) n(r) dr.$$

DFT: MATHEMATICS OR NATURAL SCIENCE?

Development presented so far was purely formal mathematics.

(though physically motivated)

DFT becomes a natural science when and only when it is used in conjunction with sufficiently simple and accurate approximations for $F[n(r)]$ or $E_{xc}[n(r)]$

These approximations come from outside DFT.

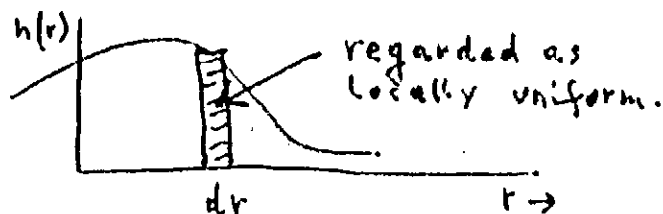
4. APPROXIMATIONS FOR $E_{xc}[n(r)]$

a. Local density approximation (LDA)

$$E_{xc}^{LDA}[n(r)] = \int E_{xc}(n(r)) n(r) dr,$$

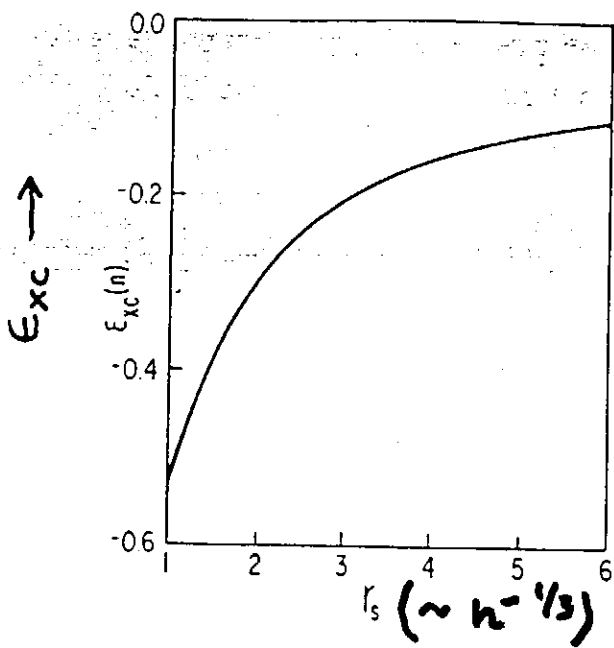
where

$E_{xc}(n) = (\text{exch./corr. energy})/\text{particle in uniform gas of density } n$



Observations:

- Gives unexpectedly good results, 0.5% - 10%
- Used in "99%" of applications to solids
- No harder than Hartree, much better
- Much easier than Hartree-Fock, typically similar or better accuracy (Exch is approximately included, correlation - absent in HF - also)



r_s related to n by

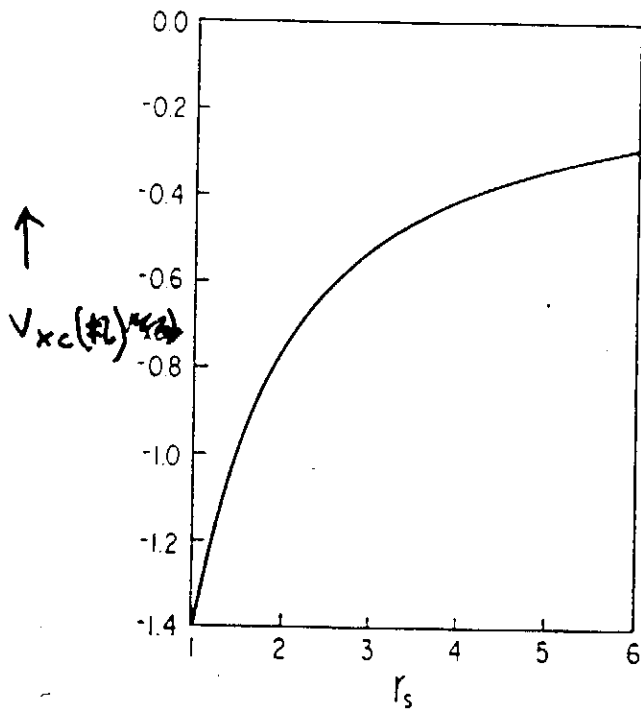
$$\frac{4\pi}{3} r_s^3 = n^{-1}$$

FIGURE 3. The exchange-correlation energy per particle of a uniform electron gas in a.u. (After Ref. 19.)

where r_s is given in terms of n by equation (26) and the function $G(x)$ is defined as

$$G(x) \equiv \frac{1}{2} [(1 + x^3)\log(1 + x^{-1}) - x^2 + x/2 - 1/3] \quad (59)$$

The great majority of all practical calculations with the KS equations have been carried out with the use of the LDA, which has yielded surprisingly good results even in cases where the density is *not* slowly varying. Later in this section we shall present a partial rationalization of the success of the LDA by the observation that it satisfies an important sum rule.



$$\frac{4\pi}{3} r_s^3 = n^{-1}$$

FIGURE 4. The exchange-correlation potential in the local density approximation in a.u. (After Ref. 19.)

Remark: DFT uses independent calculations for homogeneous, infinite systems for inhomogeneous systems.
 (It contributes nothing to the theory of homog. systems)

b. Inclusion of Gradients, $\nabla n(r)$

- Simple gradient expansion

$$E_{xc}[n(r)] = E_{xc}^{LDA}[n(r)] + \int g(n(r)) |\nabla n(r)|^2 dr + \dots$$

Not successful.

- Generalized gradient approximation (GGA)

$$E_{xc}[n(r)] = E_{xc}^{LDA}[n(r)] + \int f(n(r), |\nabla n(r)|^2) dr$$

D. Langreth, J. Perdew, A. Becke.

c. Hybrid approximations.

Combination of LDA with full exchange energy.

A. Becke

5. EXTENSIONS, GENERALIZATIONS

- a. Degenerate ground states: E_0 ; $\bar{\Psi}_0^\nu$ $\nu=1, \dots, \mu$
- b. Spin density functional theory: $n_\uparrow(r), n_\downarrow(r)$
Magnetism [KS, von Barth]
- c. Multicomponent systems: $n_\alpha(r)$, $\alpha=1, 2, \dots$
Nuclei, electron-hole drops
- d. Free energy for $T > 0$: $n(r), \Omega$ (grand potential)
Plasmas [Mermin]
- e. Excited states: $n(r) \equiv \frac{1}{M} (n_1(r) + \dots + n_M(r))$; $E_1 + E_2 + \dots + E_M$.
[Theophilou, WK]
Gross, Oliveira
- f. Orbital magnetism: $n(r) \rightarrow \{n(r), j(r)\}$ [Vignale, Rasolt]
- g. Superconductors: $n(r) = \langle \psi^\dagger(r) \psi(r) \rangle$; $\tilde{n}(r) = \langle \psi(r) \psi(r) \rangle$
[Gross, Oliveira, WK]
- h. Relativistic electrons [Rajagopal, Gross]
- i. Time-dependant phenomena: $V(r, t), n(r, t)$ [Gross]
Also: $\rightarrow E_j - E_0$ (Gross)
- j. Bosons
Surface of liquid He⁴
- k. Combination of DFT with molecular dynamics
Clusters, amorphous materials [Car and Parrinello]
- l. Formal advances [Ley, Perdew, ...]
on foundations, scaling in μ .

6. Quantitative Results (Illustrations)

- a. Atomic energies ; ionization potentials
- b. Diatomic molecules
- c. Bulk metals
- d. Metal surfaces
- e. Spin magnetism
- f. Band structures of solids

Molecular Atomization Energies, (s, p orbitals)

TABLE III. Atomization energies D_0 (kcal/mol) of first-row molecules.

	Expt. ^a	LSDA ^b		LSDA-GC ^c	
LiH	56.0	58.9	(2.9)	61.7	(5.7)
BeH	46.9	57.7	(10.8)	57.9	(11.0)
CH	79.9	88.0	(8.1)	80.4	(0.5)
CH ₂ (trip.)	179.6	202.7	(23.1)	184.6	(5.0)
CH ₂ (sing.)	170.6	188.9	(18.3)	174.9	(4.3)
CH ₃	289.2	322.0	(32.8)	295.9	(6.7)
CH ₄	392.5	435.7	(43.2)	397.7	(5.2)
NH	79.0	91.0	(12.0)	86.7	(7.7)
NH ₂	170.0	196.6	(26.6)	181.1	(11.1)
NH ₃	276.7	316.8	(40.1)	285.1	(8.4)
OH	101.3	118.3	(17.0)	100.8	(-0.5)
H ₂ O	219.3	253.8	(34.5)	222.4	(3.1)
HF	135.2	156.7	(21.5)	136.7	(1.5)
Li ₂	24.0	23.1	(-0.9)	21.1	(-2.9)
LiF	137.6	154.2	(16.6)	138.8	(1.2)
C ₂ H ₂	388.9	443.6	(54.7)	387.6	(-1.3)
C ₂ H ₄	531.9	601.8	(69.9)	532.4	(0.5)
C ₂ H ₆	666.3	749.7	(83.4)	665.8	(-0.5)
CN	176.6	217.1	(40.5)	182.7	(6.1)
HCN	301.8	350.8	(49.0)	306.7	(4.9)
CO	256.2	295.9	(39.7)	253.4	(-2.8)
HCO	270.3	325.0	(54.7)	274.6	(4.3)
H ₂ CO	357.2	417.6	(60.4)	359.8	(2.6)
CH ₃ OH	480.8	555.7	(74.9)	480.9	(0.1)
N ₂	225.1	264.1	(39.0)	230.6	(5.5)
N ₂ H ₄	405.4	483.8	(78.4)	413.4	(8.0)
NO	150.1	196.2	(46.1)	154.3	(4.2)
O ₂	118.0	172.4	(54.4)	124.8	(6.8)
H ₂ O ₂	252.3	319.0	(66.7)	255.0	(2.7)
F ₂	36.9	76.7	(39.8)	40.2	(3.3)
CO ₂	381.9	465.9	(84.0)	381.4	(-0.5)

^a Expt.—from Refs. 14 and 15.^b LSDA—local spin-density approximation [Eq. (8)].^c LSDA-GC—post-LSDA gradient corrected [Eq. (11)].

A. Becke

Molecular Atomization Energies, 2.

TABLE IV. Atomization energies D_0 (kcal/mol) of second-row molecules.

	Expt. ^a	LSDA ^b	LSDA-GC ^c
SiH ₂ (sing.)	144.4	159.1 (14.7)	150.0 (5.6)
SiH ₂ (trip.)	123.4	139.7 (16.3)	128.4 (5.0)
SiH ₃	214.0	233.8 (19.8)	218.8 (4.8)
SiH ₄	302.8	328.0 (25.2)	308.3 (5.5)
PH ₂	144.7	165.6 (20.9)	152.4 (7.7)
PH ₃	227.4	255.1 (27.7)	232.1 (4.7)
H ₂ S	173.2	197.3 (24.1)	174.3 (1.1)
HCl	102.2	116.4 (14.2)	101.7 (-0.5)
Na ₂	16.6	19.9 (3.3)	16.3 (-0.3)
Si ₂	74.0	92.5 (18.5)	73.4 (-0.6)
P ₂	116.1	142.4 (26.3)	114.7 (-1.4)
S ₂	100.7	134.4 (33.7)	100.4 (-0.3)
Cl ₂	57.2	82.7 (25.5)	51.7 (-5.5)
NaCl	97.5	102.8 (5.3)	91.0 (-6.5)
SiO	190.5	222.4 (31.9)	189.1 (-1.4)
CS	169.5	200.3 (30.8)	165.4 (-4.1)
SO	123.5	166.2 (42.7)	126.6 (3.1)
ClO	63.3	104.1 (40.8)	64.9 (1.6)
ClF	60.3	94.2 (33.9)	59.8 (-0.5)
Si ₂ H ₆	500.1	549.4 (49.3)	501.3 (1.2)
CH ₃ Cl	371.0	424.9 (53.9)	367.4 (-3.6)
CH ₃ SH	445.1	508.6 (63.5)	441.6 (-3.5)
HOCl	156.3	203.3 (47.0)	155.6 (-0.7)
SO ₂	254.0	332.5 (78.5)	249.9 (-4.1)

^a Expt.—from Refs. 14 and 15.

^b LSDA—local spin-density approximation [Eq. (8)].

^c LSDA-GC—post-LSDA gradient corrected [Eq. (11)].

A. Becke

Present state of art for molecular binding energies (1996) ^{15"}

Hybrid + GGA (Becke)

Standard set of 56 molecules (no transition metals)

$\langle \text{SD} \rangle \sim 2.5 \text{ kcal/mole}$

Best CI calculations:

$\langle \text{SD} \rangle \sim 1 \text{ kcal/mole}$

Concluding Remarks.

1. Traditional methods (HF+CI) very successful + accurate for small systems ($N_{at} \leq 10$).
Can be systematically improved but encounter an exponential wall
2. DFT less accurate (1-10%) for small systems but can be applied to much larger systems ($N_{at} \leq 10^2 - 10^3$)
Improvements not as systematic (or routine) but continuing
3. The 2 points of view ($\Psi(r_1, \dots, r_N)$ and $n(r)$) are complementary and, I believe, enrich physics and chemistry
4. Current areas of progress in DFT include
 - a) Electronic Edge Structure
 - b) Van der Waals-type energies.
 - c) Continuing improvements of $E_{xc}[n(r)]$.