

From ab initio methods to density-functional theory

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A CMA–CTCC workshop on computational quantum mechanics

CTCC, Department of Chemistry, University of Oslo, Norway

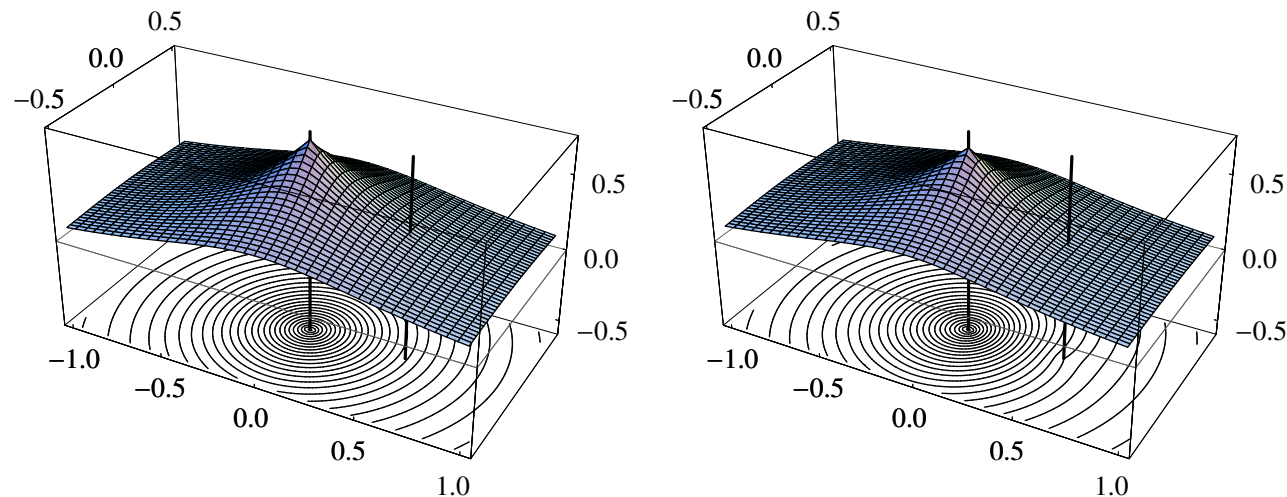
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History of quantum chemistry

- Quantum mechanics has been applied to chemistry since the 1920s
 - early accurate work on He and H₂
 - semi-empirical applications to larger molecules
- An important development was that of *ab initio theory*
 - Hartree–Fock (HF) self-consistent field (SCF) theory (1960s)
 - configuration-interaction (CI) theory (1970s)
 - multiconfigurational SCF (MCSCF) theory (early 1980s)
 - many-body perturbation theory (1980s)
 - coupled-cluster theory (late 1980s)
- Coupled-cluster theory is the most successful wave-function theory
 - introduced from nuclear physics
 - size extensive
 - hierarchical
 - the exact solution can be approached in systematic manner
 - high cost, near-degeneracy problems
- Density-functional theory (DFT) emerged during the 1990s

The Hartree–Fock approximation

- The Hartree–Fock model—the fundamental approximation of wave-function theory
 - each electron moves in the mean field of all other electrons
 - provides an uncorrelated description: average rather than instantaneous interactions
 - gives rise to the concept of molecular orbitals
 - typical errors: 0.5% in the energy; 1% in bond distances, 5%–10% in other properties
 - forms the basis for more accurate treatments
- The Hartree–Fock and exact wave functions in helium:



- concentric Hartree–Fock contours, reflecting an uncorrelated description
- in reality, the electrons see each other and the contours become distorted

Electron correlation and virtual excitations

- **electron correlation:**
 - to improve upon the Hartree–Fock model, we must take into account the instantaneous interactions among the electrons
 - in real space, the electrons are constantly being scattered by **collisions**
 - in the orbital picture, these collisions manifest themselves as **excitations** from occupied to virtual (unoccupied) spin orbitals
- **double excitations:**
 - the most important events are collisions between two electrons
 - in the orbital picture, such an event corresponds to an excitation from two occupied to two virtual spin orbitals, known as **pair excitations** or **double excitations**
- Consider the following **double-excitation operator**:

$$\hat{X}_{ij}^{ab} = t_{ij}^{ab} a_b^\dagger a_a^\dagger a_i a_j$$

- the amplitude t_{ij}^{ab} represents the probability that the electrons in ϕ_i and ϕ_j will interact and be excited to ϕ_a and ϕ_b
- by applying $1 + \hat{X}_{ij}^{ab}$ to the Hartree–Fock state, we obtain an improved, **correlated description** of the electrons:

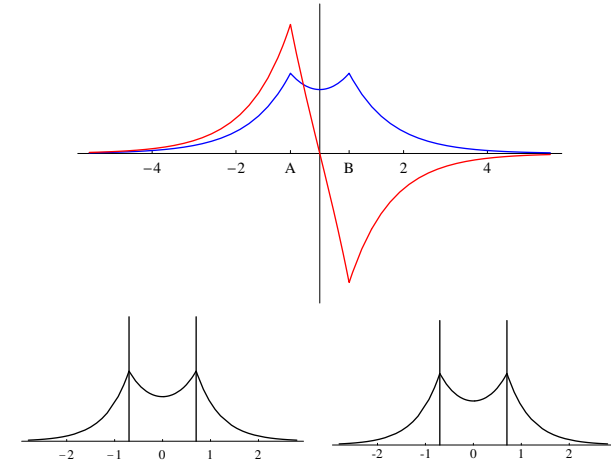
$$|\text{HF}\rangle \rightarrow (1 + \hat{X}_{ij}^{ab})|\text{HF}\rangle$$

Example: electron correlation in H₂

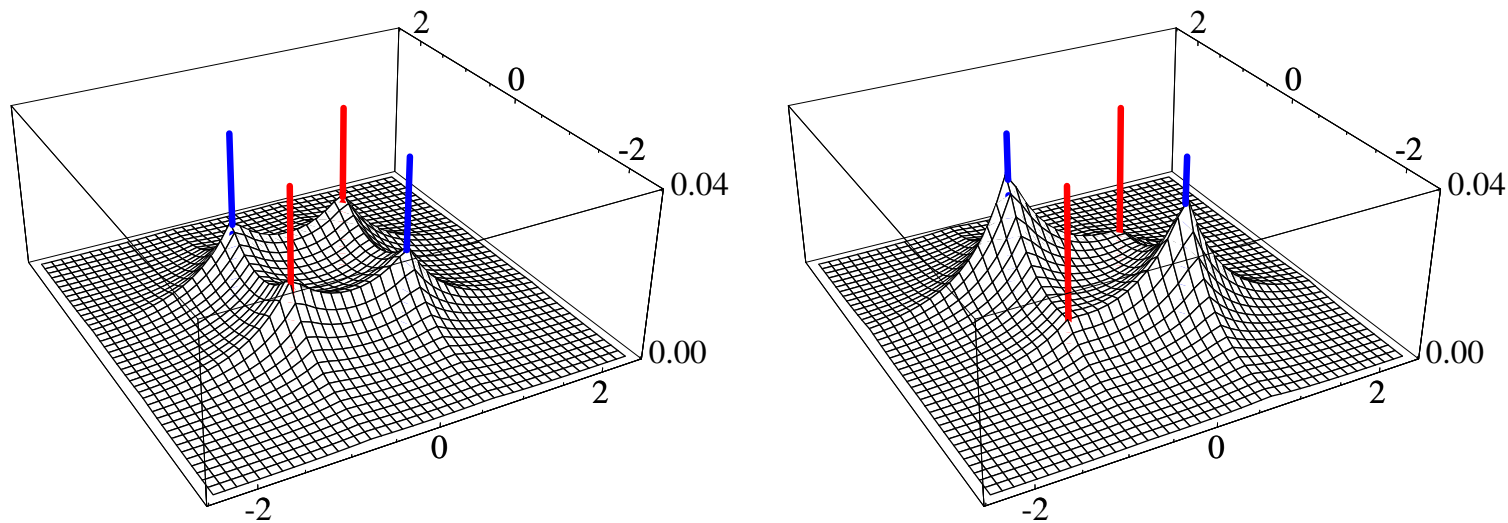
- Consider the effect of a double excitation in H₂:

$$|1\sigma_g^2\rangle \rightarrow (1 + \hat{X}_{gg}^{uu})|1\sigma_g^2\rangle = |1\sigma_g^2\rangle - 0.11|1\sigma_u^2\rangle$$

- The one-electron density $\rho(z)$ is hardly affected:



- The two-electron density $\rho(z_1, z_2)$ changes dramatically:



Coupled-cluster theory

- In **coupled-cluster (CC) theory**, we generate the correlated state from the HF reference state by applying all possible excitation operators

$$|\text{CC}\rangle = \underbrace{\left(1 + \hat{X}_i^a\right)}_{\text{singles}} \cdots \underbrace{\left(1 + \hat{X}_{ij}^{ab}\right)}_{\text{doubles}} \cdots \underbrace{\left(1 + \hat{X}_{ijk}^{abc}\right)}_{\text{triples}} \cdots \underbrace{\left(1 + \hat{X}_{ijkl}^{abcd}\right)}_{\text{quadruples}} \cdots |\text{HF}\rangle$$

- with each excitation, there is an associated **probability amplitude** $t_{ijk\dots}^{abc\dots}$
- **single excitations** represent orbital adjustments rather than interactions
- **double excitations** are particularly important, arising from pair interactions
- **higher excitations** should become progressively less important
- This classification provides a **hierarchy of ‘truncated’ CC wave functions**:
 - CCS, CCSD, CCSDT, CCSDTQ, CCSDTQ5, ...
 - errors are typically reduced by a factor of three to four at each new level
- Lower-order excitations work in tandem to produce higher-order excited configurations

$$\left(1 + \hat{X}_{ij}^{ab}\right) \left(1 + \hat{X}_{kl}^{cd}\right) |\text{HF}\rangle = |\text{HF}\rangle + \hat{X}_{ij}^{ab} |\text{HF}\rangle + \hat{X}_{kl}^{cd} |\text{HF}\rangle + \hat{X}_{ij}^{ab} \hat{X}_{kl}^{cd} |\text{HF}\rangle$$

- the important thing is to parameterize the excitations rather than the resulting states

Basis sets of Gaussian functions

- In our calculations, we expand the molecular orbitals in one-electron Gaussian-type functions (GTOs):

$$G_{ijk}(r_A, \alpha) = x_A^i y_A^j z_A^k \exp(-\alpha r_A^2)$$

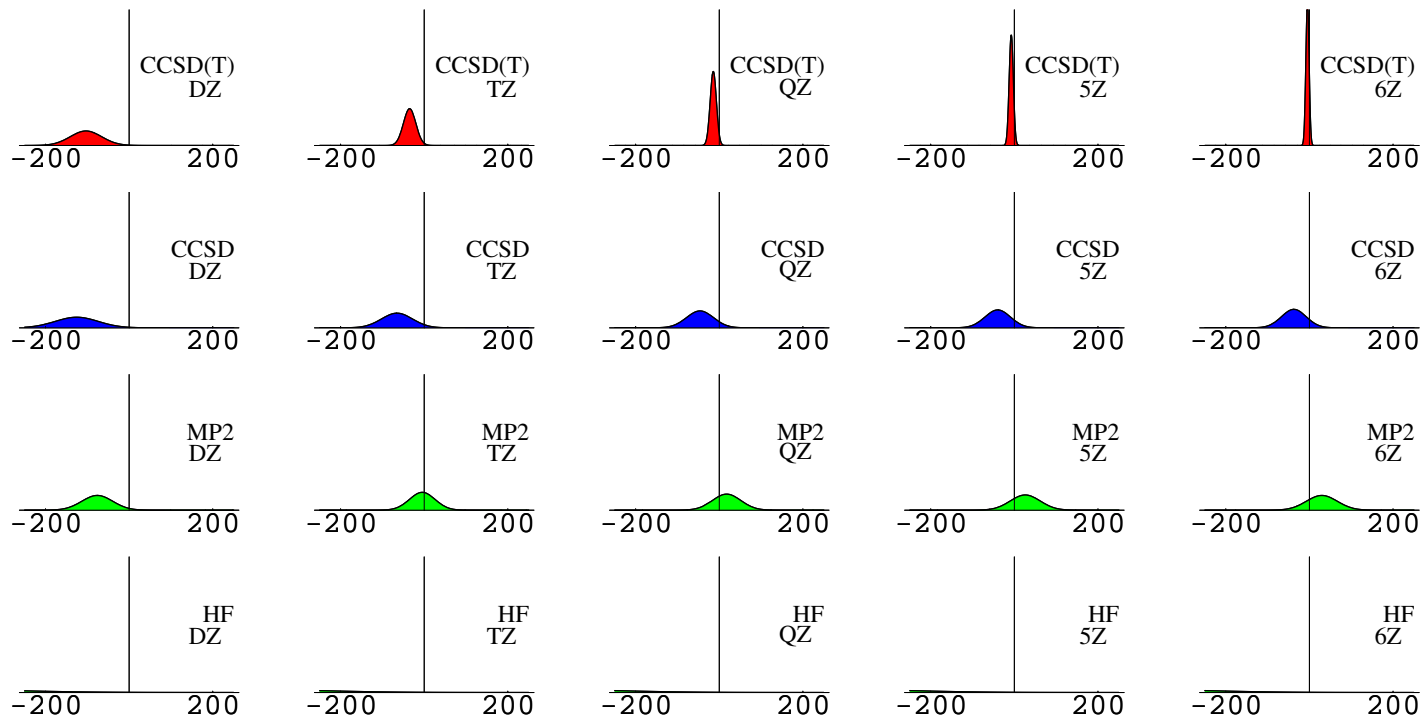
- Basis sets of increasing size:
 - minimal or single-zeta (SZ) basis sets:
 - * one set of GTOs for each occupied atomic shell ($2s1p$)
 - * gives a rudimentary description of electron structure
 - double-zeta (DZ) basis sets:
 - * two sets of GTOs for each occupied atomic shell ($3s2p1d$)
 - * sufficient for a qualitative description of the electron system
 - triple-zeta (TZ), quadruple-zeta (QZ) and larger basis sets:
 - * needed for a quantitative description of the electronic system
- The number of GTOs per atom increases rapidly:

SZ	DZ	TZ	QZ	5Z	6Z
5	14	30	55	91	140

- Large basis sets are needed to generate a flexible virtual space!

The two-dimensional chart of quantum chemistry

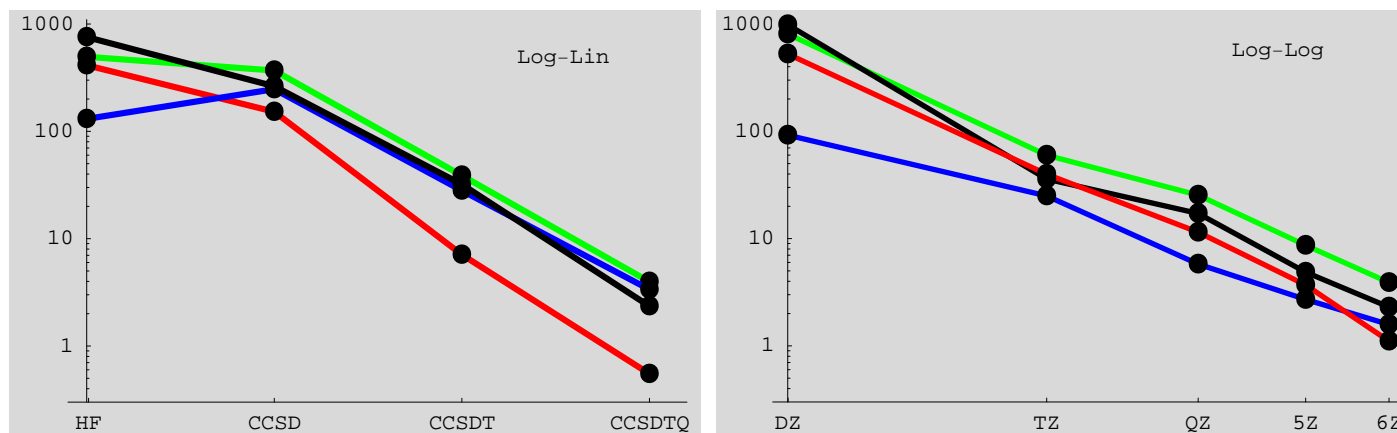
- The quality of *ab initio* calculations is determined by the description of
 1. the N -electron space (wave-function model);
 2. the one-electron space (basis set).
- Normal distributions of errors in AEs (kJ/mol)



- The errors are systematically reduced by going up in the hierarchies

Energy contributions to atomization energies (kJ/mol)

- Contributions of each CC excitation level (left) and AO basis-set shell (right)



– color code: **HF**, **N₂**, **F₂**, and **CO**

- The excitation-level convergence is approximately linear (log–linear plot)
 - each new excitation level reduces the error by about an order of magnitude
 - the contributions from quintuples are negligible (about 0.1 kJ/mol)
- The basis-set convergence is much slower (log–log plot)
 - each shell contributes an energy proportional to X^{-4} where X is the cardinal number
 - a similarly small error (0.1 kJ/mol) requires $X > 10$
 - clearly, we must choose our orbitals in the best possible manner

CC convergence: bond distances (pm)

	RHF	SD	T	Q	5	rel.	theory	exp.	err.
HF	89.70	1.67	0.29	0.02	0.00	0.01	91.69	91.69	0.00
N ₂	106.54	2.40	0.67	0.14	0.03	0.00	109.78	109.77	0.01
F ₂	132.64	6.04	2.02	0.44	0.03	0.05	141.22	141.27	-0.05
CO	110.18	1.87	0.75	0.04	0.00	0.00	112.84	112.84	0.00

CC convergence: harmonic constants ω_e (cm⁻¹)

	RHF	SD	T	Q	5	rel.	theory	exp.	err.
HF	4473.8	-277.4	-50.2	-4.1	-0.1	-3.5	4138.5	4138.3	0.2
N ₂	2730.3	-275.8	-72.4	-18.8	-3.9	-1.4	2358.0	2358.6	-0.6
F ₂	1266.9	-236.1	-95.3	-15.3	-0.8	-0.5	918.9	916.6	2.3
CO	2426.7	-177.4	-71.7	-7.2	0.0	-1.3	2169.1	2169.8	0.7

The local kinetic energy

- Consider the local energy of the helium atom

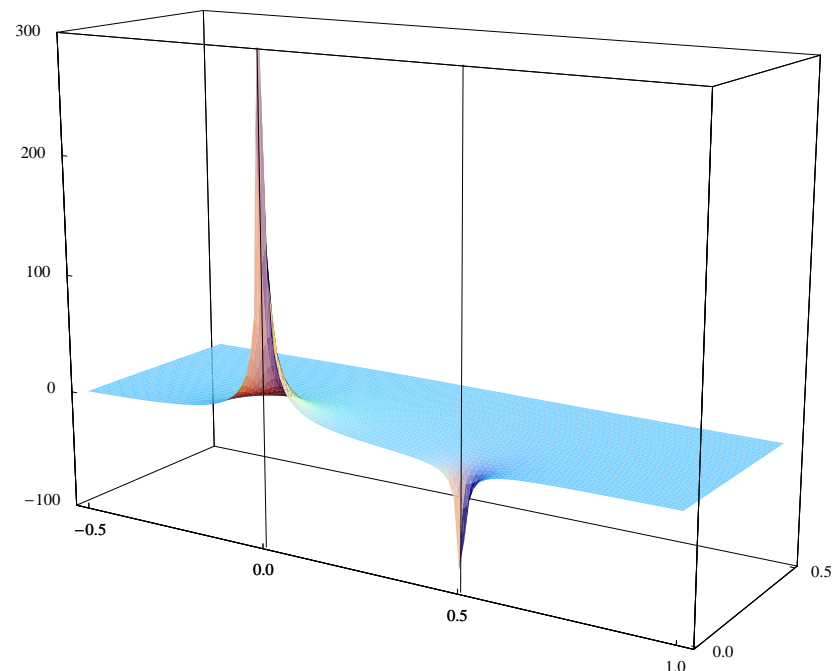
$$E_{\text{loc}} = (H\Psi)/\Psi \quad \leftarrow \text{constant for exact wave function}$$

- The electronic Hamiltonian has singularities at points of coalescence

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

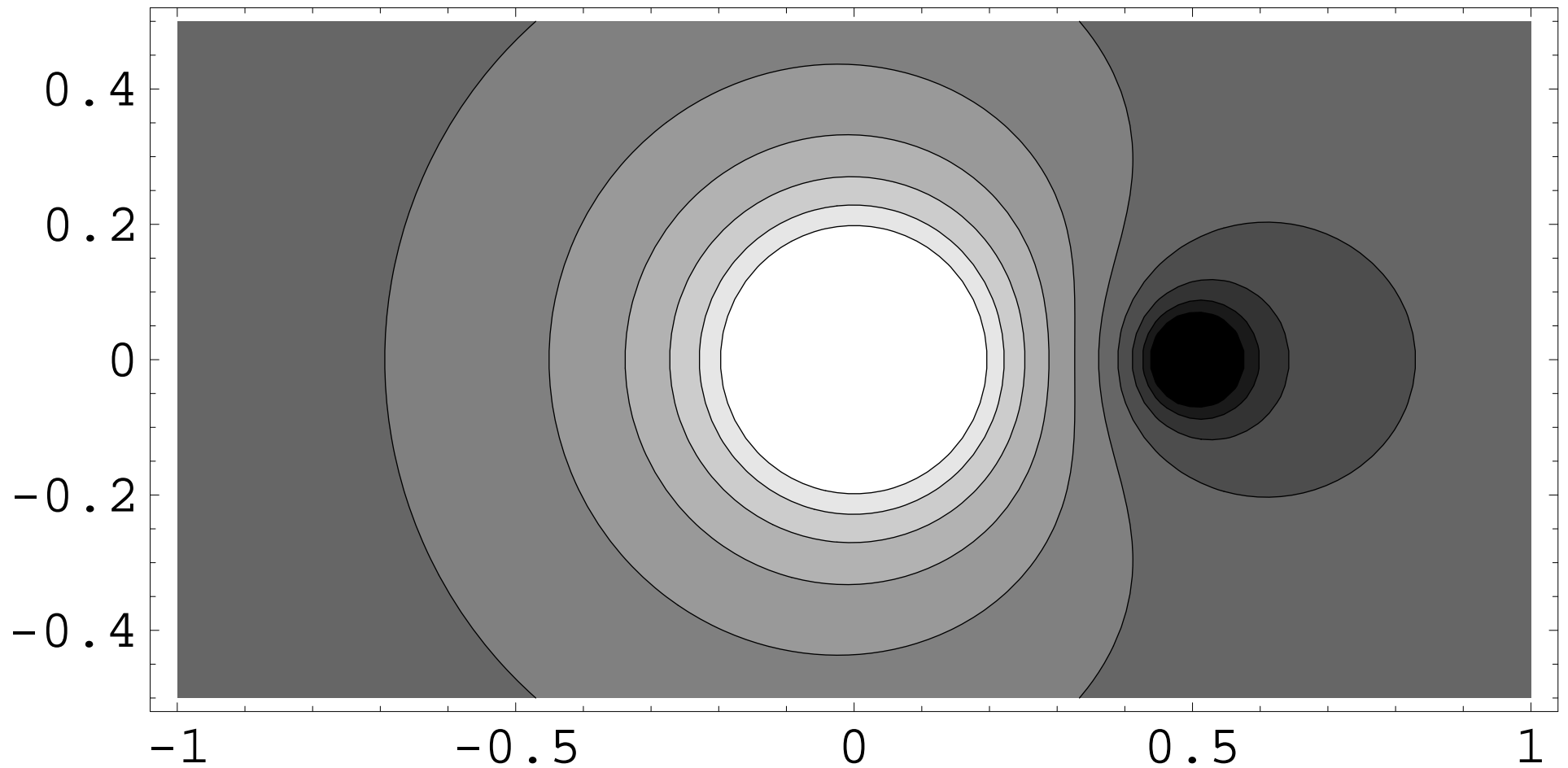
– the infinite potential terms must be canceled by infinite kinetic terms at coalescence

- Local kinetic energy in the helium atom
 - positive around the nucleus
 - negative around the second electron
- Negative kinetic energy counterintuitive
 - classical forbidden region
 - internal “tunneling”
 - w. f. decays towards the singularity
 - the Coulomb hole



The Coulomb hole: the forbidden region

- Each electron is surrounded by a classically forbidden region: the Coulomb hole
 - without a good description of this region, our results will be inaccurate

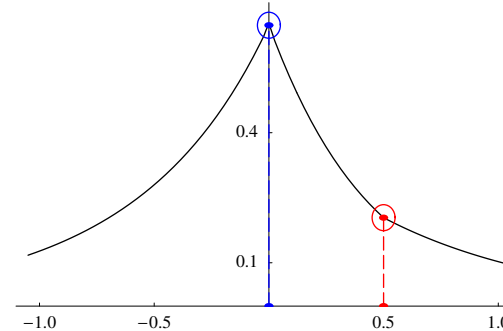


The electron cusp and the Coulomb hole

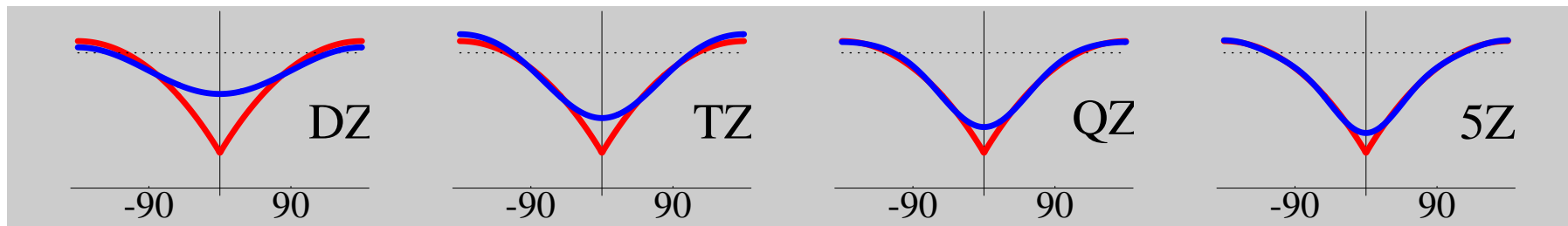
- The behaviour of the wave function at coalescence was established by Slater (1928)
 - nuclear and electronic cusp conditions

$$\left(\frac{\partial\Psi}{\partial r_i}\right)_{r_i=0,\text{ave}} = -Z\Psi(r_i=0)$$

$$\left(\frac{\partial\Psi}{\partial r_{12}}\right)_{r_{12}=0,\text{ave}} = \frac{1}{2}\Psi(r_{12}=0)$$



- The electronic cusp condition implies the existence of a **Coulomb hole**
 - its description is awkward without the use of r_{ij} in the wave function:



- standard wave functions use orbitals and do not contain r_{ij} explicitly

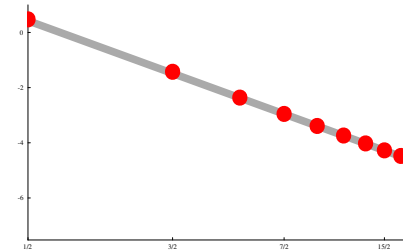
The principal expansion and correlation-consistent basis sets

- The energy contribution from each AO in large CI calculations on helium:

$$\varepsilon_{nlm} \approx n^{-6} \quad \leftarrow \text{Carroll } et \text{ al. (1979)}$$

- The principal expansion:** include all AOs belonging to the same shell simultaneously, in order of increasing principal quantum number n :

$$\varepsilon_n \approx n^2 n^{-6} = n^{-4}$$



- The error in the energy is equal to the contributions from all omitted shells:

$$\Delta E_X \approx \sum_{n=X+1}^{\infty} n^{-4} \approx X^{-3} \approx N^{-1} \approx T^{-1/4}$$

- Each new digit in the energy therefore costs 10000 times more CPU time!

$$1 \text{ minute} \quad \rightarrow \quad 1 \text{ week} \quad \rightarrow \quad 200 \text{ years}$$

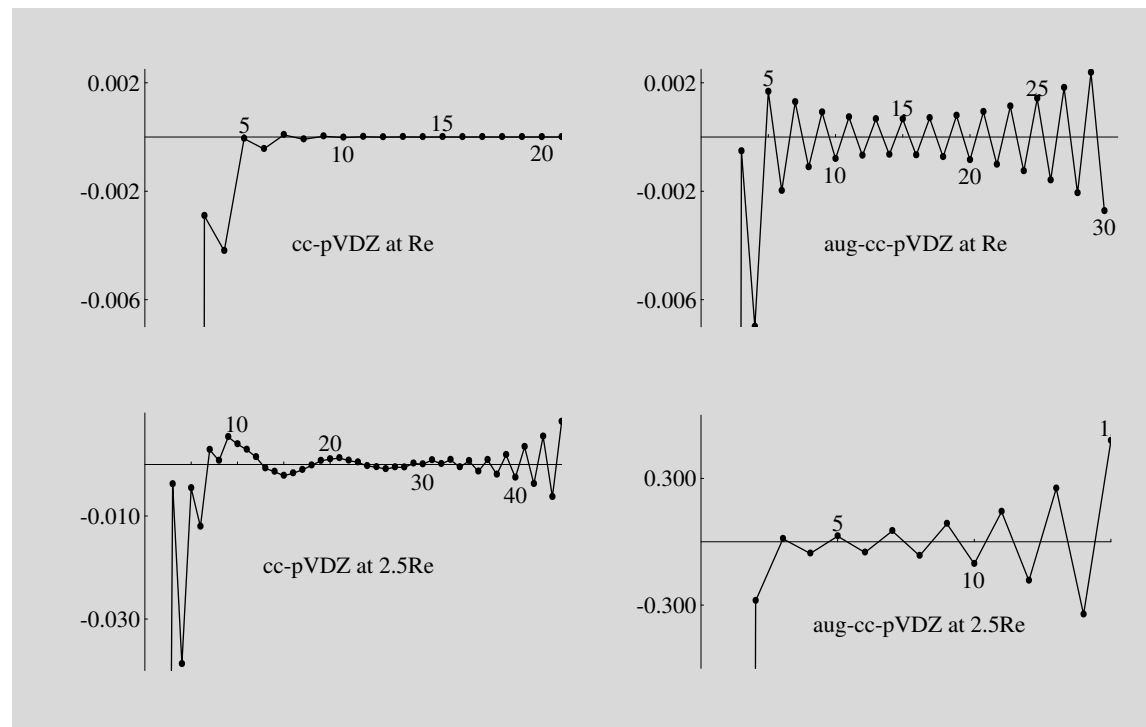
- Exploit the smooth convergence $E_{\infty} = E_X + AX^{-3}$ to extrapolate to basis-set limit:

$$E_{\infty} = \frac{X^3 E_X - Y^3 E_Y}{X^3 - Y^3}$$

mE _h	DZ	TZ	QZ	5Z	6Z	R12
plain	194.8	62.2	23.1	10.6	6.6	1.4
extr.		21.4	1.4	0.4	0.5	

Many-body perturbation theory: approximate coupled-cluster theory

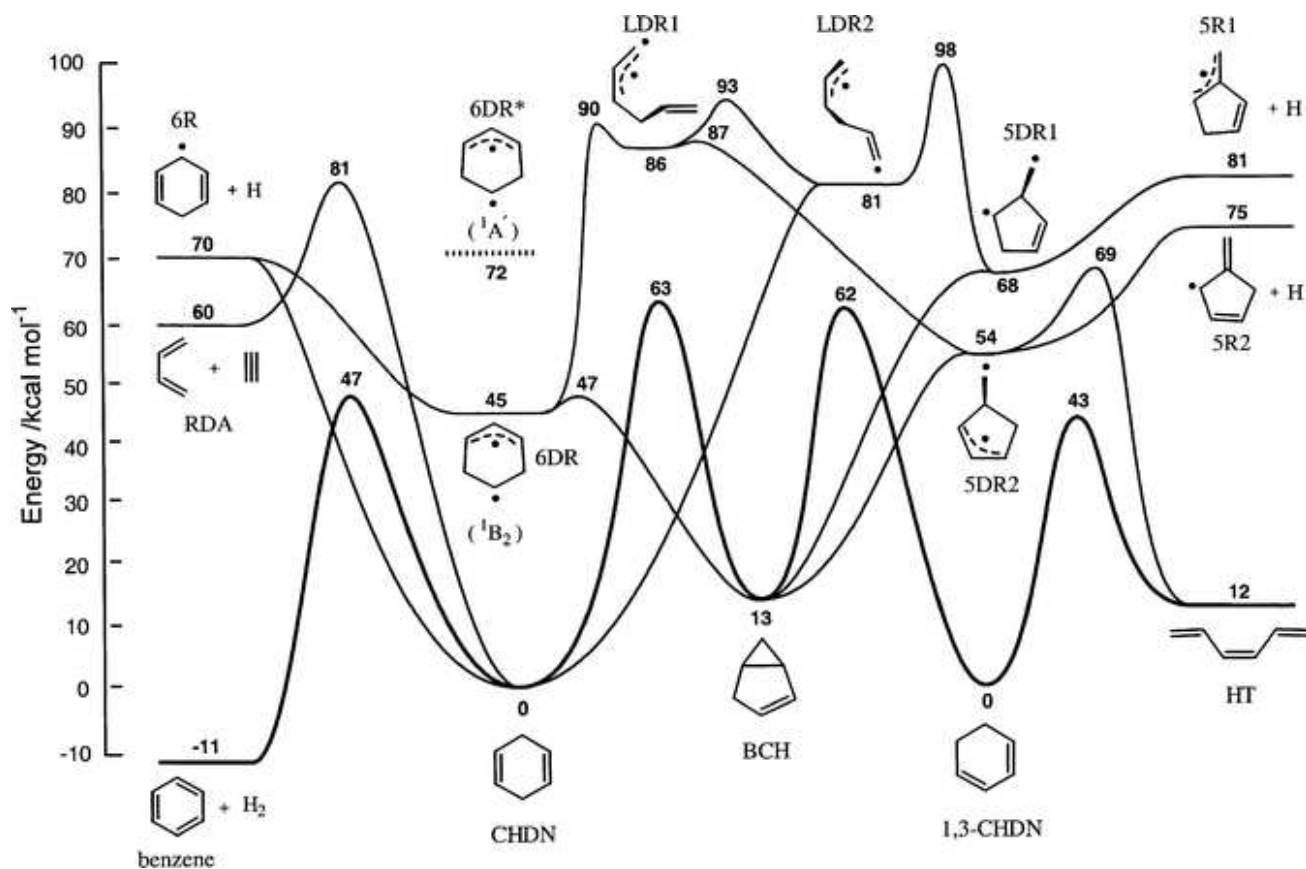
- Coupled-cluster amplitudes may be estimated by **perturbation theory**
- Caveat: the resulting perturbation series is frequently divergent, even in simple cases
 - here are some examples for the HF molecule (10 electrons):



- However, to lowest order, perturbational corrections are very useful and popular
 - **MP2** (approximate CCSD) and **CCSD(T)** (approximate CCSDT)
 - correlation effects are typically overestimated, leading to fortuitously good results

The emergence of DFT

- The traditional methods of quantum chemistry are capable of high accuracy
 - nevertheless, most calculations are performed using density-functional theory (DFT)
- What is the reason for the popularity of DFT?
 - the standard methods are (at least for high accuracy) very expensive



Density-functional theory

- For chemists, we view the electronic energy as a functional $E[v]$ of the potential

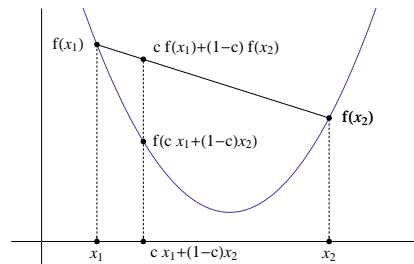
$$v(\mathbf{r}) = \sum_K \frac{Z_K}{r_K} \quad \text{Coulomb potential}$$

- In standard QC, we determine $E[v]$ by solving (approximately) the Schrödinger equation

$$E[v] = \min_{\Psi} \langle \Psi | \hat{H}[v] | \Psi \rangle \quad \text{variation principle}$$

- However, the negative ground-state energy $\bar{E}[v]$ is a convex functional of the potential

$$\bar{E}(cv_1 + (1-c)v_2) \geq c\bar{E}(v_1) + (1-c)\bar{E}(v_2), \quad 0 \leq c \leq 1 \quad \text{convexity}$$



- The energy may then be expressed in terms of its Legendre–Fenchel transform

$$F[\rho] = \sup_v (E[v] - \int v(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r}) \quad \text{energy as a functional of density}$$

$$E[v] = \inf_{\rho} (F[\rho] + \int v(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r}) \quad \text{energy as a functional of potential}$$

- the universal density functional $F[\rho]$ is the central quantity in DFT

The conjugate energy functionals $E[v]$ and $F[\rho]$

- As chemists we may choose to work in terms of $E[v]$ or $F[\rho]$:

$$F[\rho] = \sup_v \left(E[v] - \int v(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r} \right) \quad \text{definition of the universal density functional}$$

$$E[v] = \inf_\rho \left(F[\rho] + \int v(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r} \right) \quad \text{Hohenberg–Kohn variation principle}$$

- the relationship is the same as between Hamiltonian and Lagrangian mechanics
- The potential $v(\mathbf{r})$ and the density $\rho(\mathbf{r})$ are **conjugate variables**
 - they belong to **dual linear spaces** such that $\int v(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r}$ is finite
 - they satisfy the **reciprocal relations**

$$\delta F[\rho]/\delta\rho(\mathbf{r}) = -v(\mathbf{r}), \quad \delta E[v]/\delta v(\mathbf{r}) = \rho(\mathbf{r})$$

- In **molecular mechanics (MM)**, we work in terms of $E[v]$
 - parametrization of energy as a function of bond distances, angles etc.
 - widely used for large systems (in biochemistry)
- In **density-functional theory (DFT)**, we work in terms of $F[\rho]$
 - the exact functional is unknown but useful approximations exist
 - more accurate than molecular mechanics, widely used in chemistry
- Neither method involves the direct solution of the Schrödinger equation

Kohn–Sham theory

- The Hohenberg–Kohn variation principle

$$E[v] = \min_{\rho} \left(F[\rho] + \int v(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r} \right)$$

- the functional form of $F[\rho]$ is **unknown**—the kinetic energy is most difficult

$$F[\rho] = \min_{\Psi \rightarrow \rho} \left\langle \Psi \left| -\frac{1}{2} \sum_i \nabla^2 + \sum_{i>j} r_{ij}^{-1} \right| \Psi \right\rangle$$

- A **noninteracting system** can be solved exactly, at low cost, by introducing orbitals

$$F[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho], \quad \rho(\mathbf{r}) = \sum_i \phi_i(\mathbf{r})^* \phi_i(\mathbf{r})$$

where the contributions are

$$T_s[\rho] = -\frac{1}{2} \sum_i \int \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) \, d\mathbf{r} \quad \text{noninteracting kinetic energy}$$

$$J[\rho] = \iint \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)r_{12}^{-1} \, d\mathbf{r}_1 d\mathbf{r}_2 \quad \text{Coulomb energy}$$

$$E_{xc}[\rho] = F[\rho] - T_s[\rho] - J[\rho] \quad \text{exchange–correlation energy}$$

- In **Kohn–Sham theory**, we solve a noninteracting problem in an effective potential

$$\left[-\frac{1}{2} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}), \quad v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + v_J(\mathbf{r}) + \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}$$

- $v_{\text{eff}}(\mathbf{r})$ is adjusted such that the noninteracting density is equal to the true density
- it remains to specify the exchange–correlation functional $E_{xc}[\rho]$

The exchange–correlation functional

- The exact exchange–correlation functional is unknown
 - we must rely on approximations
- Local-density approximation (LDA)
 - XC functional modeled after the uniform electron gas (which is known exactly)

$$E_{xc}^{\text{LDA}}[\rho] = \int f(\rho(\mathbf{r})) \, d\mathbf{r} \quad \text{local dependence on density}$$

- widely applied in condensed-matter physics
 - not sufficiently accurate to compete with traditional methods of quantum chemistry
- Generalized-gradient approximation (GGA)
 - introduce a dependence also on the density gradient

$$E_{xc}^{\text{GGA}}[\rho] = \int f(\rho(\mathbf{r}), \nabla\rho(\mathbf{r})) \, d\mathbf{r} \quad \text{local dependence on density and its gradient}$$

- Becke's gradient correction to exchange (1988) changed the situation
 - the accuracy became sufficient to compete in chemistry
 - indeed, surprisingly high accuracy for energetics

Exchange–correlation functionals (plural)

- The **exchange–correlation energy** contains several contributions

$$E_{\text{xc}}[\rho] = F[\rho] - T_{\text{s}}[\rho] - J[\rho]$$

- exchange (dominant), correlation, kinetic-energy correction

- The **Dirac exchange** with **Becke's gradient correction**:

$$E_{\text{X}} = \sum_{\sigma} \int \rho_{\sigma} (\mathcal{E}_{\sigma}^{\text{Dirac}}(\mathbf{r}) + \mathcal{E}_{\sigma}^{\text{Becke}}(\mathbf{r})) \, \text{d}\mathbf{r}$$

$$\mathcal{E}_{\sigma}^{\text{Dirac}}(\mathbf{r}) = -\frac{3}{4} \left(\frac{6}{\pi}\right)^{1/3} \rho_{\sigma}^{1/3}(\mathbf{r})$$

$$\mathcal{E}_{\sigma}^{\text{Becke}}(\mathbf{r}) = -\frac{\beta \rho_{\sigma}^{1/3}(\mathbf{r}) s_{\sigma}^2(\mathbf{r})}{1 + 6\beta s_{\sigma}(\mathbf{r}) \sinh^{-1} s_{\sigma}(\mathbf{r})}, \quad s_{\sigma}(\mathbf{r}) = \frac{|\nabla \rho_{\sigma}(\mathbf{r})|}{\rho_{\sigma}^{4/3}(\mathbf{r})}$$

- the Becke correction contains the **adjustable parameter** $\beta = 0.0042$
- fitted to HF exchange of noble-gas atoms

- The Becke correction is often used with the **LYP (Lee–Yang–Parr) correlation functional**
 - contains four adjustable parameters, fitted to the helium-atom correlation energy
- The resulting functional is known under the acronym BLYP
 - a bewildering variety of functionals has been developed
 - sometimes chosen to satisfy **exact conditions**, other times **fitted to data**

A plethora of exchange–correlation functionals

Table 1. MADs (all energies in eV) for various level of theory for the extended G2 set

Method	G2(MAD)				H-Ne, E_{tot}	TM ΔE	He ₂ , $\Delta E(R_e)$	Ne ₂ , $\Delta E(R_e)$	(H ₂ O) ₂ , $D_e(R_{O\dots O})$
	ΔH_f	IP	EA	PA					
HF	6.47	1.036	1.158	0.15	4.49	1.09	Unbound	Unbound	0.161 (3.048)
G2 or best <i>ab initio</i>	0.07 ^a	0.053 ^b	0.057 ^b	0.05 ^b	1.59 ^c	0.19 ^d	0.0011 (2.993)^e	0.0043 (3.125)^e	0.218 (2.912)^f
LDA (SVWN)	3.94 ^a	0.665	0.749	0.27	6.67	0.54 ^g	0.0109 (2.377)	0.0231 (2.595)	0.391 (2.710)
GGA									
BP86	0.88 ^a	0.175	0.212	0.05	0.19	0.46	Unbound	Unbound	0.194 (2.889)
BLYP	0.31 ^a	0.187	0.106	0.08	0.19	0.37 ^g	Unbound	Unbound	0.181 (2.952)
BPW91	0.34 ^a	0.163	0.094	0.05	0.16	0.60	Unbound	Unbound	0.156 (2.946)
PW91PW91	0.77	0.164	0.141	0.06	0.35	0.52	0.0100 (2.645)	0.0137 (3.016)	0.235 (2.886)
mPWPW ^h	0.65	0.161	0.122	0.05	0.16	0.38	0.0052 (2.823)	0.0076 (3.178)	0.194 (2.911)
PBEPBE ⁱ	0.74 ⁱ	0.156	0.101	0.06	1.25	0.34	0.0032 (2.752)	0.0048 (3.097)	0.222 (2.899)
XLYP ^j	0.33	0.186	0.117	0.09	0.95	0.24	0.0010 (2.805)	0.0030 (3.126)	0.192 (2.953)
Hybrid methods									
BH & HLYP ^k	0.94	0.207	0.247	0.07	0.08	0.72	Unbound	Unbound	0.214 (2.905)
B3P86 ^l	0.78 ^a	0.636	0.593	0.03	2.80	0.34	Unbound	Unbound	0.206 (2.878)
B3LYP ^m	0.13 ^a	0.168	0.103	0.06	0.38	0.25 ^g	Unbound	Unbound	0.198 (2.926)
B3PW91 ⁿ	0.15 ^a	0.161	0.100	0.03	0.24	0.38	Unbound	Unbound	0.175 (2.923)
PW1PW ^o	0.23	0.160	0.114	0.04	0.30	0.30	0.0066 (2.660)	0.0095 (3.003)	0.227 (2.884)
mPW1PW ^p	0.17	0.160	0.118	0.04	0.16	0.31	0.0020 (3.052)	0.0023 (3.254)	0.199 (2.898)
PBE1PBE ^q	0.21 ⁱ	0.162	0.126	0.04	1.09	0.30	0.0018 (2.818)	0.0026 (3.118)	0.216 (2.896)
O3LYP ^r	0.18	0.139	0.107	0.05	0.06	0.49	0.0031 (2.860)	0.0047 (3.225)	0.139 (3.095)
X3LYP ^s	0.12	0.154	0.087	0.07	0.11	0.22	0.0010 (2.726)	0.0028 (2.904)	0.216 (2.908)
Experimental	—	—	—	—	—	—	0.0010 (2.970)^t	0.0036 (3.091)^t	0.236 ^u (2.948) ^v

ΔH_f , heat of formation at 298 K; PA, proton affinity; E_{tot} , total energies (H-Ne); TM ΔE , s to d excitation energy of nine first-row transition metal atoms and nine positive ions. Bonding properties [ΔE or D_e in eV and (R_e) in Å] are given for He₂, Ne₂, and (H₂O)₂. The best DFT results are in boldface, as are the most accurate answers [experiment except for (H₂O)₂].

Reaction Enthalpies (kJ/mol)

	B3LYP		CCSD(T)		exp.
$\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_4$	-543	1	-543	1	-544(2)
$\text{C}_2\text{H}_2 + \text{H}_2 \rightarrow \text{C}_2\text{H}_4$	-208	-5	-206	-3	-203(2)
$\text{C}_2\text{H}_2 + 3\text{H}_2 \rightarrow 2\text{CH}_4$	-450	-4	-447	-1	-446(2)
$\text{CO} + \text{H}_2 \rightarrow \text{CH}_2\text{O}$	-34	-13	-23	-2	-21(1)
$\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_2$	-166	-2	-165	-1	-164(1)
$\text{F}_2 + \text{H}_2 \rightarrow 2\text{HF}$	-540	23	-564	-1	-563(1)
$\text{O}_3 + 3\text{H}_2 \rightarrow 3\text{H}_2\text{O}$	-909	24	-946	-13	-933(2)
$\text{CH}_2\text{O} + 2\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$	-234	17	-250	1	-251(1)
$\text{H}_2\text{O}_2 + \text{H}_2 \rightarrow 2\text{H}_2\text{O}$	-346	19	-362	3	-365(2)
$\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$	-268	4	-273	-1	-272(1)
$\text{HCN} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{NH}_2$	-320	0	-321	-1	-320(3)
$\text{HNO} + 2\text{H}_2 \rightarrow \text{H}_2\text{O} + \text{NH}_2$	-429	15	-446	-2	-444(1)
$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	-211	33	-244	0	-244(1)
$2\text{CH}_2 \rightarrow \text{C}_2\text{H}_4$	-845	-1	-845	-1	-844(3)