20. (a) N. Ishii and T. Shimizu, *Chem. Phys. Lett.*, 1994, **225**, 462–466; (b) N. Ishii and T. Shimizu, *Chem. Phys. Lett.*, 1995, **235**, 614–616.
21. L. A. Eriksson, O. L. Malkina, V. G. Malkin, and D. R. Salahub, *J. Chem. Phys.*, 1994, **100**, 5066–5075.
22. (a) V. Barone, *J. Chem. Phys.*, 1994, **101**, 6834–6838; (b) V. Barone, 'Recent Advances in Density Functional Methods, Part I', ed. D. P. Chong, World Scientific, Singapore, 1995, pp. 287–334.
23. J. Kong, L. A. Eriksson, and R. J. Boyd, *Chem. Phys. Lett.*, 1994, **217**, 24–30.
24. C. W. Bauschlicher, Jr. and H. Partridge, *Chem. Phys. Lett.*, 1995, **240**, 533–540.
25. B. J. Smith and L. Radom, *Chem. Phys. Lett.*, 1994, **231**, 345–351.
26. H. F. Hameka, 'Advanced Quantum Chemistry', Addison-Wesley, New York, 1963.
27. M. Schindler and W. Kutzelnigg, *J. Am. Chem. Soc.*, 1983, **105**, 1360–1370.
28. K. Wolinski, J. F. Hinton, and P. Pulay, *J. Am. Chem. Soc.*, 1990, **112**, 8251–8260.
29. T. A. Keith and R. F. W. Bader, *Chem. Phys. Lett.*, 1993, **210**, 223–231.
30. G. Schreckenbach and T. Ziegler, *J. Phys. Chem.*, 1995, **99**, 606–611.
31. V. G. Malkin, O. L. Malkina, M. E. Casida, and D. R. Salahub, *J. Am. Chem. Soc.*, 1994, **116**, 5898–5908.
32. J. R. Cheeseman, G. W. Trucks, T. A. Keith, and M. J. Frisch, *J. Chem. Phys.*, 1996, **104**, 5497–5509.
33. J. Guan, P. Duffy, J. T. Carter, D. P. Chong, K. C. Casida, M. E. Casida, and M. Wrinn, *J. Chem. Phys.*, 1993, **98**, 4753–4765.
34. G. D. Zeiss, W. R. Scott, N. Suzuki, D. P. Chong, and S. R. Langhoff, *Mol. Phys.*, 1979, **37**, 1543–1572.
35. N. Matsuzawa and D. A. Dixon, *J. Phys. Chem.*, 1994, **98**, 2545–2554.
36. J. M. L. Martin, J. El-Yazal, and J.-P. Francois, *Mol. Phys.*, 1995, **86**, 1437–1450.
37. L. Fan and T. Ziegler, *J. Chem. Phys.*, 1991, **95**, 7401–7408.
38. B. G. Johnson and M. J. Frisch, *Chem. Phys. Lett.*, 1993, **216**, 133–140.
39. (a) D. P. Chong, *Chin. J. Phys.*, 1992, **30**, 115–127; (b) D. P. Chong and D. Papousek, *J. Mol. Spect.*, 1992, **155**, 167–176; (c) D. P. Chong and D. Papousek, *Chin. J. Phys.*, 1992, **30**, 829–839; (d) D. P. Chong and A. Bree, *Chem. Phys. Lett.*, 1993, **210**, 443–447; (e) D. P. Chong, *Chem. Phys. Lett.*, 1994, **220**, 102–108; (f) D. Papousek, Z. Papouskova, and D. P. Chong, *J. Phys. Chem.*, 1995, **99**, 15387–15395; (g) D. Papousek, Z. Papouskova, and D. P. Chong, *Ind. J. Chem.*, 1995, **A34**, 760–764; (h) D. Papousek, Z. Papouskova, and D. P. Chong, *J. Mol. Struct.*, 1996, **363**, 115–124.
40. L. Fan and T. Ziegler, *J. Chem. Phys.*, 1992, **96**, 9005–9012.
41. A. Stirling, *J. Chem. Phys.*, 1996, **104**, 1254–1262.
42. A. R. Williams, R. A. deGroot, and C. B. Sommers, *J. Chem. Phys.*, 1975, **63**, 628–631.
43. J. F. Janak, *Phys. Rev. B*, 1978, **18**, 7165–7168.
44. D. P. Chong, *J. Chem. Phys.*, 1995, **103**, 1842–1845.
45. D. P. Chong, C.-H. Hu, and P. Duffy, *Chem. Phys. Lett.*, 1996, **249**, 491–495.
46. C.-H. Hu and D. P. Chong, *Chem. Phys.*, 1997, **216**, 99–104.
47. K. A. Peterson and T. H. Dunning, Jr., *J. Phys. Chem.*, 1995, **99**, 3898–3901.
48. C.-H. Hu and D. P. Chong, *Chem. Phys. Lett.*, 1996, **262**, 729–732.
49. G. A. Jeffrey and W. Saenger, 'Hydrogen Bonding in Biological Structures', Springer-Verlag, Berlin, 1991.
50. F. Sim, A. St-Amant, I. Papai, and D. R. Salahub, *J. Am. Chem. Soc.*, 1992, **114**, 4391–4400.
51. V. Barone, C. Adamo, and F. Lelj, *J. Chem. Phys.*, 1995, **102**, 364–370.
52. S. F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553–566.
53. K. Kim and K. D. Jordan, *J. Phys. Chem.*, 1994, **98**, 10089–10094.
54. D. A. Estrin, L. Paglieri, G. Corongiu, and E. Clementi, *J. Phys. Chem.*, 1996, **100**, 8701–8711.
55. S. S. Xantheas, *J. Chem. Phys.*, 1995, **102**, 4505–4517.
56. C. Lee, H. Chen, and G. Fitzgerald, *J. Chem. Phys.*, 1995, **102**, 1266–1269.
57. S. Kristyán and P. Pulay, *Chem. Phys. Lett.*, 1994, **229**, 175–180.
58. J. M. Pérez-Jordá and A. D. Becke, *Chem. Phys. Lett.*, 1995, **233**, 134–137.
59. O. Wiest, K. A. Black, and K. N. Houk, *J. Am. Chem. Soc.*, 1994, **116**, 10336–10337.
60. E. Goldstein, B. Beno, and K. N. Houk, *J. Am. Chem. Soc.*, 1996, **118**, 6036–6043.
61. Q. Zhang, R. Bell, and N. Truong, *J. Phys. Chem.*, 1995, **99**, 592–599.

Density Functional Theory (DFT), Hartree–Fock (HF), and the Self-consistent Field

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1 INTRODUCTION

The self-consistent field (SCF) concept is the keystone of modern computational chemistry, encompassing both the Hartree-Fock (HF) and density functional (DFT) theories. Its vocabulary has become established as an essential part of the language by which chemists communicate and it has had a profound impact on our understanding of chemistry at the microscopic level, whether organic or inorganic. Molecular orbitals and orbital energies, Walsh and Tanabe–Sugano diagrams, Woodward–Hoffmann rules, donor–acceptor models, even the assertion that benzene has π-electrons, all stem directly from the portrait of electronic structure that SCF theory paints.

Many branches of physics deal with systems of mutually interacting particles. When the number of particles is very small, it is usually possible to treat them exactly, or nearly so. A simple pendulum, a hydrogen atom and an orbiting satellite are examples of such systems. When the number of particles is very large, statistical methods can be used and, in favorable cases, the resulting treatments can also be nearly exact. A cylinder of CO_2 gas, a liquid crystal, and a bacterial colony are all complicated systems that yield to statistical modeling. In between, however, lies a harder class of problems in which there are numerous particle–particle interactions but for which statistical arguments yield insufficient accuracy. It is in this arena that SCF theories have frequently played a vital role.

The sun and its n attendant planets, interacting gravitationally, constitute such a problem. If we assume a static sun at the origin, the total energy E of the system can be written as

$$E = \frac{1}{2}\sum_i^n m_i \dot{\mathbf{r}}_i^2 - \sum_i^n \frac{GMm_i}{|\mathbf{r}_i|} - \sum_i^n \sum_{j>i}^n \frac{Gm_i m_j}{|\mathbf{r}_i - \mathbf{r}_j|} \qquad (1)$$

where M is the solar mass and m_i and $\mathbf{r}_i$ are the mass and position of the ith planet. The terms in equation (1) correspond to the kinetic energy of the planets, the sun–planet potential energy, and the planet–planet potential energies, respectively. The third term, however, couples the motions of the planets and renders this a complicated mechanical system. Understanding the consequent planetary motions became a famous pursuit in the history of celestial mechanics, one that attracted the attention of generations of mathematical physicists including Newton and Laplace. Many variants are possible, but there are broadly three approaches to the treatment of this problem.

In a crude approach, after noting that the sun is much more massive than the planets and that the sun–planet interactions will therefore usually be much larger than the planet–planet interactions, we ignore the third term completely. This dramatically simplifies the problem because it decouples the planetary motions and factorizes the problem into n completely independent problems, each involving the motion of only one planet. As Kepler discovered, and Newton proved, this affords an elliptic orbit for each planet. One cannot, however, feel completely comfortable with this solution. By our cavalier removal of the most difficult term in equation (1), it is quite conceivable that we have lost some essential elements of the physics. After all, the very existences of Neptune and Pluto were originally inferred from observed deviations from ellipticity in the orbit of Uranus!

Alternatively, at the other extreme, we abandon all intuitive simplifications and engage the services of a powerful computer to solve (1) directly. Because of the complexity of the problem, the only way to obtain the solution is via a dynamic simulation using extremely small time steps. Provided the simulation is performed with due care, this approach will probably generate accurate planetary motions and may indicate the importance, or otherwise, of the planet–planet interactions. However, the inelegant numerical description that results will be very difficult to interpret and, in all likelihood, will yield very little physical insight.

There is, however, a middle ground. Suspecting that, while smaller than the sun–planet interactions, the planet–planet interactions cannot be ignored completely, we could suggest that the latter be treated in an approximate fashion by replacing the difficult third term in (1) by something resembling the second one. While it is clearly true that a given planet moves under the influence of the sun, we could posit that it is also justifiable to suppose that it moves under the average influence of all of the other planets and write

$$E^{(0)} = \frac{1}{2}\sum_i^n m_i \dot{\mathbf{r}}_i^2 - \sum_i^n \frac{GMm_i}{|\mathbf{r}_i|} - \sum_i^n Gm_i v(|\mathbf{r}_i|) \qquad (2)$$

This step greatly simplifies the original problem, for the explicit planet–planet interactions have disappeared and have been replaced by the average field v in which all the planets move. Ideally, we would like all of the physics of the true planet–planet interactions somehow to be embedded within this field but this may be asking for more than can reasonably be expected. We expect that a few of the finer details have probably been lost between (1) and (2).

It is clear that this approximation, like the much cruder one described earlier, factorizes the original problem into n independent one-planet problems. Moreover, if we know the field v, we can solve these problems to find the n planetary orbits $\psi_i(\mathbf{r})$. However, v must depend on the $\psi_i(\mathbf{r})$ and it appears that we have created a chicken-and-egg paradox! Fortunately, this difficulty can be resolved simply by stipulating that the field generated from the orbits must also generate those orbits. This requirement defines a self-consistent field method.

The analogies between a solar system and a molecular system are not difficult to see. If the molecule has n electrons with coordinates $\mathbf{r}_i$, the total energy of the electrons is found by solving the Schrödinger Equation $\mathbf{H}\Psi = E\Psi$ where the Hamiltonian[1] is given by

$$\mathbf{H} = -\frac{1}{2}\sum_i^n \nabla_i^2 + \sum_i^n V(\mathbf{r}_i) + \sum_i^n \sum_{j>i}^n \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \qquad (3)$$

and $V(\mathbf{r})$ is the classical electrostatic potential due to the nuclei. The similarity between (1) and (3) is clear and the task of solving the Schrödinger Equation is analogous to solving the planetary problem. In particular, it is the third term in (3) that greatly complicates matters by coupling the motions of the electrons. However, if we suppose that each electron moves in the average field due to all of the others, we can decouple the problem and solve self-consistently for the n one-electron orbitals $\psi_i(\mathbf{r})$ using the much simpler Hamiltonian

$$\mathbf{H}^{(0)} = -\frac{1}{2}\sum_i^n \nabla_i^2 + \sum_i^n V(\mathbf{r}_i) + \sum_i^n v(\mathbf{r}_i) \qquad (4)$$

What form of the average potential v should we use? This is a critical question because we would like v to contain implicitly information about the complicated physics that underlies the electron–electron interactions. Long ago,[2] Hohenberg and Kohn proved the remarkable result that there exists a unique form of the potential which, if used self-consistently, actually yields the exact Schrödinger energy E. In other words, if this potential is used, the SCF methodology is no longer an approximation. This is wonderful news but, unfortunately, this 'ultimate' potential is unknown. Consequently, SCF theorists have had to devote many years of research to the construction of approximate potentials and, at least for now, must remain content with imperfect approximations to their elusive ideal.

Every approximate potential that is devised defines a new SCF method and, over the years, very many have been proposed. Some were introduced at the dawn of the quantum

mechanics revolution, others more recently. Some have been devised by physicists, others by chemists. Some are most conveniently discussed in terms of the electron orbitals, others in terms of the spin densities, still others in terms of the total electron density. Our aim, however, is to offer a presentation of these various methods that is as unified as possible, in order to emphasize particularly the features that they all share.

Hartree–Fock theory and density functional theory are both SCF models and share many conceptual and computational features. Yet they are all too rarely presented together. This can be traced to the fact that, historically, they have not been studied by the same people and this dichotomy has been detrimental to the development of both. Fortunately, late in the 20th century, the two schools have recognized their common heritage and fruitfully liaised.

Our presentation will be largely operational. There is a wealth of more detailed material to which the reader should turn for more information. The classic primers by Szabo and Ostlund[3] and Parr and Yang[4] are excellent; the former for its treatment of HF and the correlation models that proceed from it, the latter as a thought-provoking introduction to DFT. Beyond these lie more advanced treatises such as that by Dreizler and Gross.[5]

2 THE ENERGY EXPRESSION IN QUANTUM CHEMISTRY

It is conceptually useful to partition the total electronic energy E of a chemical system as

$$E = E_T + E_V + E_J + E_X + E_C \tag{5}$$

and computer programs that find approximate solutions to chemical Schrödinger equations usually calculate these pieces independently. The terms in equation (5) are as follows: the first, E_T, is the kinetic energy of the electrons; the second, E_V, is the Coulomb energy of the electrons due to their attraction to the nuclei; the third, E_J, is the Coulomb energy that the electrons would have in their own field if they moved independently (which they don't) and if each electron repelled itself (which it doesn't); the remaining contribution, $E_{XC} \equiv E_X + E_C$, corrects for these two false assumptions.

It is worth commenting further on E_{XC}. Like planets, electrons perturb one another when they approach closely and, as a consequence, their motions cannot possibly be independent. Moreover, unlike planets, electrons with the same spin avoid one another particularly keenly and, because of the Pauli Exclusion Principle, are never found at the same point in space. The non-independence of motion arising from the Pauli Principle is known as Fermi correlation. The consequent stabilization, along with a correction for the self-repulsions of the electrons, is known as the exchange energy E_X, and is the major part of E_{XC}. A smaller component, E_C, arises primarily from correlation between the motions of electrons with different spins.

It should be noted carefully that the five terms in (5) are of entirely different magnitudes. E_T, E_V, and E_J constitute most of E, E_X is a much smaller term, and E_C is a very small correction. In a Ne atom, for example, E_T, E_V, E_J, E_X, and E_C are +129, 312, +66, 12, and 0.4 au.

The next three sections contain brief descriptions of some of the important or popular formulae that have been used to estimate the terms in (5), emphasizing the relationships between them. It is important to recognize that the expressions for E_V and E_J are common to all quantum chemical methods. Thus, it is the formulae used for E_T, E_X, and E_C that distinguish the various SCF methods from one another.

Figure 1 depicts some of the methodological developers of mainstream quantum chemistry. It is clear that four interrelated families of methods have emerged. They are distinguished by their use of the orbitals ψ_i and density ρ to find E_T and E_{XC}. Specifically, we have:

1. Hartree–Fock-based theories, wherein E_T and E_{XC} both come from the ψ_i.
2. Adiabatic connection theories, wherein E_T comes from the ψ_i and E_{XC} from the ψ_i and ρ.
3. Kohn–Sham theories, wherein E_T comes from the ψ_i and E_{XC} from ρ.
4. Pure density functional theories, wherein E_T and E_{XC} both come from ρ.

Figure 1 shows the marriage of Hartree's ideas with pure DFT to yield Kohn–Sham theory[6,7] and the later marriage of Fock's ideas with this to yield adiabatic connection theory[8] to have been pivotal points in the evolution of modern quantum chemical thought.

3 ORBITAL FUNCTIONALS

A functional is a mathematical device that maps objects onto numbers. In the context of quantum chemistry, an orbital functional is a well-defined procedure that takes the orbitals of a system and returns an energy.

3.1 The Hartree Kinetic Functional

In 1928, Hartree introduced[9] the SCF philosophy to the embryonic field of quantum chemistry. He proposed a model in which the ith electron in an atom moves completely independently of the others in an orbital $\psi_i(\mathbf{r})$. Within this uncorrelated picture, the total kinetic energy is simply the sum of the kinetic energies of the individual electrons which, as Schrödinger had shown, is given by

$$E_T^{H28} = -\frac{1}{2}\sum_i^n \int \psi_i(\mathbf{r})\nabla^2\psi_i(\mathbf{r})\,d\mathbf{r} \tag{6}$$

The early applications of Hartree's independent-electron model were confined to atoms but, by 1930, Lennard-Jones, Mulliken, and Hund had shown that the model can be readily extended to molecules by allowing the $\psi_i(\mathbf{r})$ to delocalize over several atoms. This marked the birth of molecular orbital theory. It should be emphasized that equation (6) does not yield the exact kinetic energy (except in one-electron systems) because, in reality, the electrons do not move independently of one another. Their motions are correlated and, because they try to avoid one another, $E_T^{H28} < E_T$. Nonetheless, H28 turns out to be a surprisingly good approximation.

3.2 The Self-interaction-correction Functional

Although his original work did not make explicit reference to exchange energy, Hartree's treatment rigorously excludes

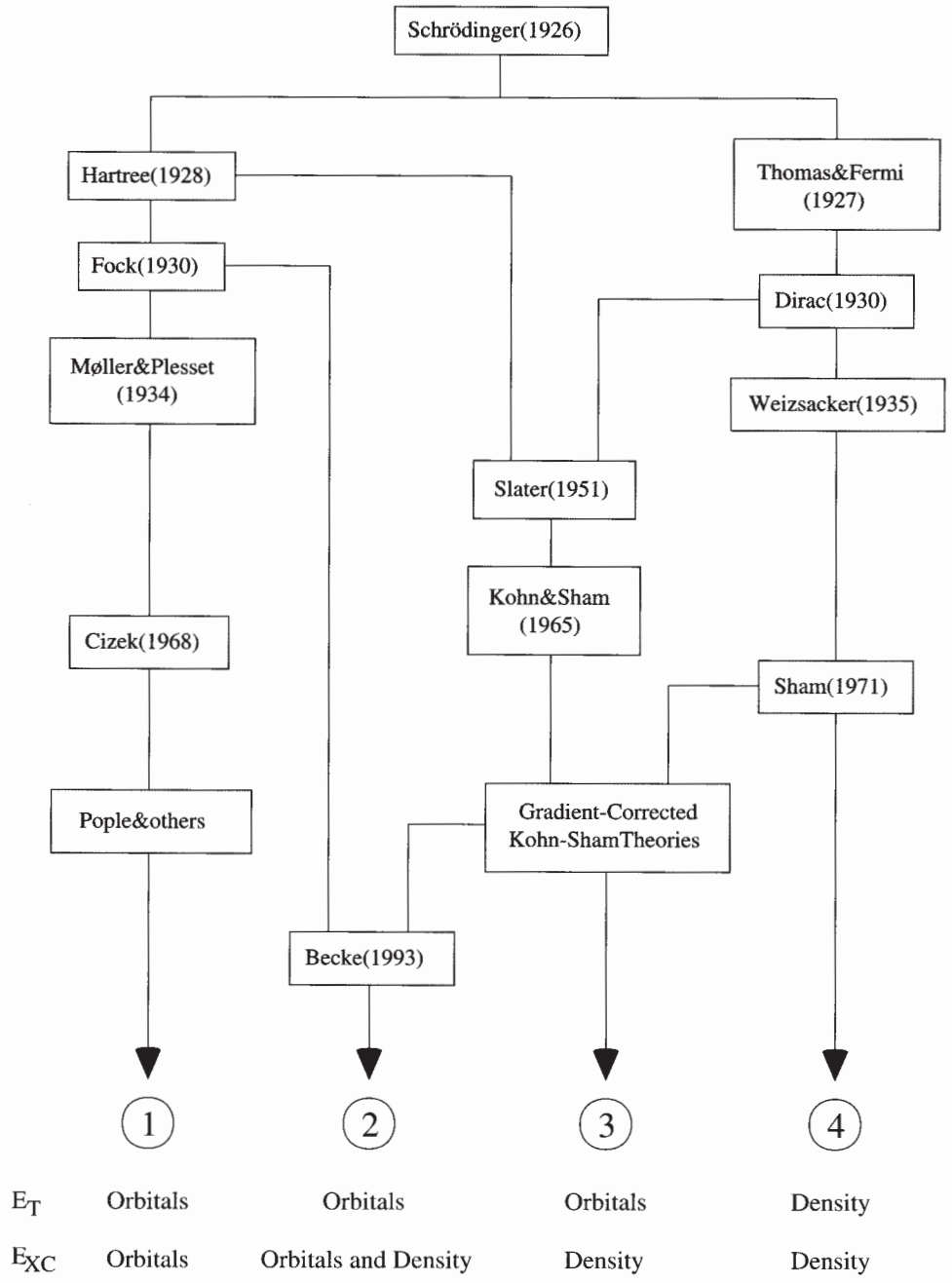

Figure 1 The evolution and classification of quantum chemical methods

spurious self-interactions of the electrons. If couched in terms of the partition in equation (5), this exclusion becomes the exchange functional

$$E_X^{SIC} = -\frac{1}{2}\sum_i^n \int\int \frac{\psi_i^2(\mathbf{r}_1)\psi_i^2(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\,d\mathbf{r}_1\,d\mathbf{r}_2 \qquad (7)$$

The major weakness of SIC is that it is not invariant to unitary transformations of the $\psi_i(\mathbf{r})$.

3.3 The Fock Exchange Functional

In 1930, Fock pointed out[10] that the Hartree wavefunction violates the Pauli Exclusion Principle because it is not properly antisymmetric. He showed that this deficiency can be remedied by antisymmetrizing the wavefunction but that electrons of the same spin now avoid one another, a phenomenon called Fermi correlation or exchange. Fock showed that this treatment corresponds to the exchange functional

$$E_X^{F30} = -\frac{1}{2}\sum_i^n\sum_j^n \int\int \frac{\psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_1)\psi_i(\mathbf{r}_2)\psi_j(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\,d\mathbf{r}_1\,d\mathbf{r}_2 \qquad (8)$$

The SIC, which arises automatically when antisymmetric wavefunctions are used, is embedded in F30 but additional terms ensure that F30 is invariant to unitary transformations of the $\psi_i(\mathbf{r})$.

3.4 Orbital Correlation Functionals

Each of the various Møller–Plesset, coupled-cluster, and configuration interaction methods (all of which yield estimates of the correlation energy E_C and are described in other articles) can be viewed as an orbital correlation functional.

4 DENSITY FUNCTIONALS BASED ON THE UNIFORM ELECTRON GAS

In 1965, Hohenberg and Kohn proved[2] that each of the contributions to the total energy in equation (5) can be expressed as a functional of the total electron density

$$\rho(\mathbf{r}) = \rho_\alpha(\mathbf{r}) + \rho_\beta(\mathbf{r}) = \sum_{i\in\alpha} \psi_i^2(\mathbf{r}) + \sum_{i\in\beta} \psi_i^2(\mathbf{r}) \tag{9}$$

where the sums are over alpha (spin-up) orbitals and beta (spin-down) orbitals, respectively. This is easy to see for E_V and E_J (see following section), but it is surprising that it is also true of E_T, E_X, and E_C. However, their proof was non-constructive and we therefore do not know what these functionals are. As a result, the most pressing problem in DFT is the construction of approximate but accurate functionals for E_T, E_X, and E_C in atomic and molecular systems.

4.1 The Uniform Electron Gas

Consider the idealized system of n electrons within a cubical box of volume V throughout which there is uniformly distributed positive charge sufficient to render the system neutral. The uniform electron gas (UEG) of density $\rho = n/V$ is obtained as the limit of this system as $n, V \to \infty$. Although the UEG bears some resemblance to the 'electron sea' in metals, its chief virtue is its simplicity. Despite being a many-electron system, it is completely defined by a single variable – its density ρ – and it is relatively easy to study. It is often called 'jellium'. A detailed discussion of the properties of jellium can be found in Appendix E of Ref. 4.

4.2 The Thomas–Fermi Kinetic Functional

Soon after the 1926 Schrödinger paper, Thomas[11] and Fermi[12] derived a kinetic energy formula based on jellium. The derivation, which requires only the wavefunctions of a particle in a box (see Section 9), shows that the exact alpha kinetic energy of jellium is

$$E_T^{TF27} = \frac{3}{10}(6\pi^2)^{2/3} \int \rho_\alpha^{5/3}(\mathbf{r})\,d\mathbf{r} \tag{10}$$

When applied to atoms and molecules, TF27 yields energies that are roughly 10% smaller than those from H28. The derivation of TF27 marked the birth of density functional theory for it was the first occasion on which it had been shown that a non-electrostatic energy term can be expressed directly in terms of the density, without mentioning the wavefunction.

4.3 The Dirac Exchange Functional

Following Thomas and Fermi, Dirac showed[13] that the alpha exchange energy of jellium is

$$E_X^{D30} = -\frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3} \int \rho_\alpha^{4/3}(\mathbf{r})\,d\mathbf{r} \tag{11}$$

When applied to atoms and molecules, D30 yields energies that are roughly 10% smaller than those of F30. Unlike F30, D30 only partly removes the spurious electronic self-interactions.

4.4 The Vosko–Wilk–Nusair Correlation Functional

In 1980, Ceperley and Alder used Monte Carlo methods to find the correlation energy of jellium numerically.[14] Vosko, Wilk, and Nusair then fitted their results to obtain[15] the E_C^{VWN} correlation functional. Its somewhat complicated form is given in Appendix E of Ref. 4. Unfortunately, although (almost) exact for jellium, VWN is found to overestimate correlation energies by roughly a factor of two when applied to atoms and molecules. One can infer from this that jellium is a more successful reference system for exchange than correlation energy.

5 OTHER DENSITY FUNCTIONALS

5.1 The Nuclear-attraction Functional

The electrostatic (or Coulomb) energy of the electrons due to the nuclei can be found classically. If the ath nucleus in the system is fixed at $\mathbf{R}_a$ and has nuclear charge Z_a, then we have

$$E_V = -\sum_a^m Z_a \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_a|}\,d\mathbf{r} \tag{12}$$

where m is the total number of nuclei. Because it is exact, all SCF methods use this formula. If the density $\rho(\mathbf{r})$ can be written as a sum of Gaussian or exponential functions centered at points throughout the system, the integrals in equation (12) can be found in closed form.

5.2 The Electron-repulsion Functional

The true Coulomb energy of the electrons in their own field is extremely difficult to calculate. However, if we assume that they move independently and that each electron experiences the field due to all electrons, including itself, we are led to the classical formula

$$E_J = \frac{1}{2}\int\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\,d\mathbf{r}_1\,d\mathbf{r}_2 \tag{13}$$

Although inexact, equation (13) is a reasonable approximation and is used in almost all SCF methods; it is expected that the functional used for E_{XC} will correct most of the error in E_J. As before, if the density can be written as a sum of Gaussian or exponential functions, the integrals in equation (13) can be found in closed form.

5.3 The 'Pairs' Correlation Functional

The early work of Hylleraas on the ground states of the helium-like ions (H^-, He, Li^+, ...) revealed that the correlation energy of an electron pair is roughly 42 mHartree irrespective of the spatial extent of the pair. In contrast, because

of antisymmetry, the correlation energy of a pair of same-spin electrons is at least an order of magnitude smaller. (The correlation energy of the triplet $1s^{\alpha}2s^{\alpha}$ excited state of the helium atom, for example, is roughly 1 mHartree.) These rules of thumb have subsequently been found to be roughly true for electrons in a variety of molecules and this simple observation immediately suggests the 'Pairs' functional

$$E_C^{\text{Pairs}} = -0.084 \int \frac{\rho_\alpha(\mathbf{r})\rho_\beta(\mathbf{r})}{\rho(\mathbf{r})}\,d\mathbf{r} \tag{14}$$

This functional yields 42 mHartree for systems such as the ground-state He atom or H_2 molecule but vanishes for systems such as the triplet He atom or the H atom.

5.4 The Wigner Correlation Functional

In 1938, following a careful analysis of the behavior of correlation energies at low densities, Wigner proposed a functional that reduces to the Pairs form at high densities but which yields somewhat smaller energies for smaller densities. His original form[16] can be generalized to

$$E_C^{W38} = -4a \int \frac{\rho_\alpha(\mathbf{r})\rho_\beta(\mathbf{r})}{\rho(\mathbf{r})} \left(\frac{1}{1 + d\rho^{-1/3}(\mathbf{r})}\right) d\mathbf{r} \tag{15}$$

Various values for a and d have been explored. One choice[17] is $a = 0.04918$ and $d = 0.349$.

5.5 The von Weizsacker Kinetic Functional

It has long been recognized that the electron densities in atoms and molecules are actually far from uniform and that reference systems more sophisticated than jellium are required. The original work along these lines by von Weizsacker was based on the 'almost uniform gas' obtained by adding small density ripples to jellium. The resulting system is characterized by both its density ρ and the mean value of its density gradient $|\nabla\rho|$ and introduces a general route to the improvement of density functionals that are based on jellium.

It is convenient to discuss functionals that depend on density gradients in terms of

$$x(\mathbf{r}) = \frac{|\nabla\rho(\mathbf{r})|}{\rho^{4/3}(\mathbf{r})} \tag{16}$$

which is a dimensionless variable often called the reduced density gradient. It should be noted that $x(\mathbf{r})$ takes small values in bonding regions, larger values in core regions and very large values in the Rydberg regions of molecules. Functionals that depend on both $\rho(\mathbf{r})$ and $x(\mathbf{r})$ are known as 'gradient-corrected density functionals'.

Von Weizsacker[18] found that the kinetic energy of the 'almost uniform gas' is given by

$$E_T^{W35} = E_T^{TF27} + \frac{1}{8}\int \rho_\alpha^{5/3} x_\alpha^2\,d\mathbf{r} \tag{17}$$

and this is the original gradient-corrected density functional. It was shown subsequently that von Weizsacker's derivation was flawed and that his correction was too large by a factor of nine. If the modified functional is applied to atoms and molecules, it yields kinetic energies that are typically within 1% of those from H28. Encouraged by this, subsequent workers found the x^4 and x^6 corrections[19,20] but, unfortunately, such terms grow so rapidly in the Rydberg regions of atoms and molecules that the x^6 (and higher) corrections are infinite!

5.6 The Sham–Kleinman Exchange Functional

Following the success of the von Weizsacker approach in improving the Thomas–Fermi kinetic functional, Sham showed in 1971 that an analogous correction to the Dirac exchange functional can be derived.[21] Kleinman later demonstrated[22] that the Sham derivation was flawed and that his correction was too small by exactly 10/7. It is now agreed that the correct second-order alpha exchange functional is

$$E_X^{SK71} = E_X^{D30} - \frac{5}{(36\pi)^{5/3}}\int \rho_\alpha^{4/3} x_\alpha^2 \tag{18}$$

SK71 is the prototype gradient-corrected exchange functional. Like TF27, D30, and W35, it is an *ab initio* functional, i.e., it can be derived entirely from first principles. This distinguishes it from its more popular successors (see below) which contain semiempirical parameters. When applied to atoms and molecules, SK71 yields energies that are typically 3% smaller than those from F30.

Several workers have explored higher-order (e.g., x^4) corrections to the Dirac functional and have shown that these can be found using generalizations of the von Weizsacker method. However, the x^4 correction is not found to yield useful improvements over SK71 and, for the same reasons as those described above, the corrections become infinite beyond this.

Although SK71 yields considerably better exchange energies than D30, it can be improved further by increasing the prefactor in equation (18) by roughly a factor of two and this was originally studied by Herman et al.[23] Nonetheless, neither SK71 nor its various modified forms has been employed significantly because their potentials are unbounded in the Rydberg regions of molecules and this has been held by some workers to be a serious liability.

5.7 The Becke 88 Exchange Functional

During the 1980s, there were numerous attempts to construct a gradient-corrected exchange functional that yields accurate exchange energies for atoms. Recognizing that the divergent behavior of SK71 in Rydberg regions can be traced to the fact that its integrand grows too fast with x, several workers sought to 'damp' the x^2 for large x. The most successful attempt of this type was due to Becke, who showed[24] in 1988 that a form for the damping factor can be deduced by stipulating that the functional yield the correct exchange energy density in the Rydberg regions. The simplest reasonable functional of the required form is

$$E_X^{B88} = E_X^{D30} - b\int \rho_\alpha^{4/3} \frac{x_\alpha^2}{1 + 6\beta x_\alpha \sinh^{-1} x_\alpha}\,d\mathbf{r} \tag{19}$$

and Becke determined the semiempirical parameter $b = 0.0042$ by fitting to the F30 exchange energies of the inert gas atoms, He to Rn. We note that this value is close to that suggested by Herman et al. When applied to atoms and molecules, B88 yields exchange energies that agree very well with those from F30. The B88 functional is remarkably effective and has been widely adopted by the quantum chemistry community.

5.8 A Simpler Exchange Functional

Given the success of Becke's functional, it is reasonable to ask whether a 'damped x^2 behavior' can be achieved more neatly than it is in B88. Although x^2 grows too rapidly, it is also found that x itself grows too slowly. In 1996, an obvious compromise between these two extremes

$$E_X^{G96} = E_X^{D30} - \gamma \int \rho_\alpha^{4/3} x_\alpha^{3/2} \, d\mathbf{r} \tag{20}$$

was proposed[25] and the semiempirical parameter $\gamma = 1/137$ was determined by fitting to the F30 exchange energy of the Ar atom. Despite its simplicity and the fact that (like SK71) its potential diverges in Rydberg regions, G96 yields similar results to B88. It is surprising that such a simple functional works so well and raises important questions about the properties that an exchange functional must possess in order to be useful for chemical purposes.

5.9 The Lee–Yang–Parr Correlation Functional

The development of correlation functionals has proceeded much more slowly than that of exchange functionals. As we noted earlier, the functional (VWN) that is exact for jellium yields molecular correlation energies that are very much too large and it is thus a poor starting point for a gradient-corrected functional.

In 1988, Lee, Yang, and Parr abandoned[26] jellium in favor of the He atom, the simplest system with a non-vanishing correlation energy. Their approach was based on earlier work by Colle and Salvetti[27] and was later simplified by Miehlich et al.[28] The expressions for the spin-compensated ($\rho_\alpha = \rho_\beta$) and spin-polarized ($\rho_\alpha \neq \rho_\beta$) versions of the functional E_C^{LYP} are complicated and can be found in Ref. 28. The functional contains four parameters and these were derived from data on the He atom. When applied to atoms and molecules, the LYP functional yields very much better correlation energies than VWN and, despite possessing some theoretical deficiencies, it has become an important ingredient in many DFT procedures.

5.10 The Perdew–Wang GGA91 Functionals

Although B88 and LYP perform quite well in typical atomic and molecular calculations, both functionals fail to show certain scaling and limiting features that the unknown exact exchange-correlation functional is known to possess.[29] With these in mind, Perdew et al. developed an interesting correlation functional and a slightly modified version of B88 that corrects some of its theoretical weaknesses. Both are quite complicated and are given in Ref. 30. A number of studies indicate that the new functionals are broadly comparable to B88 and LYP.

6 ATOMIC RESULTS

Many examples of calculations utilizing SCF methods are contained in this Encyclopedia. In this section, rather than attempt a review of the performance of SCF in chemical problems, we simply sample results obtained by applying various functionals to a few small atoms. While certainly not comprehensive, such comparisons lead easily to simple conclusions.

In each case, we have applied the functional to the HF/6-311++G density of the atom and performed quadrature, if necessary, using the SG-1 grid. The results obtained are given below.

H28 may be taken as the benchmark for kinetic energies. TF27 is typically 10% smaller than H28 for atoms and thereby introduces absolute errors that are 10% of the total energies. Such errors are too large to lead to chemically useful models. W35, which is correct to second order in x, is usually within 1% of H28; it overestimates in small atoms and underestimates in larger ones. W35 has large absolute errors but these come from core, not valence, electrons.

F30 is often taken to define exchange energies. D30 underestimates by roughly 10% but, because $|E_X| \ll |E_T|$, the absolute D30 errors are usually very much smaller than those of TF27. SK71, which is correct to second order in x, systematically underestimates F30 by around 3%. B88 and G96, which were fitted to inert gas F30 values, give very good agreement with F30. Interestingly, GGA91, which is a tweaked version of B88, is generally rather worse than it.

For reference, Table 1 includes exact E_C values.[31] The MP2 functional systematically underestimates because the basis set used is deficient in functions of high angular momentum. Pairs does not perform very well because it accounts for correlation within electron pairs but not between them. W38 (with the parameters from Section 5.4) is the simplest functional that yields semiquantitatively correct energies. Both VWN and GGA91 predict non-zero E_C values in the one-electron H atom and VWN overestimates true E_C values by a factor of two. Both LYP and GGA91 energies are usually in good agreement with the exact values.

Finally, we note that the GGA91 exchange and correlation errors often partially cancel.

7 QUANTUM CHEMICAL ENERGY PROCEDURES

In Section 2, we partitioned the electronic energy E into several terms using equation (5). In Section 5, we gave formulae for two of these, E_V and E_J, in equations (12) and (13) and, in Sections 3, 4, and 5, we discussed a variety of functionals that estimate the three remaining terms, E_T, E_X, and E_C. We are thus now in a position to 'mix and match' in various ways. We are free to combine

any kinetic functional, e.g., H28, TF27, W35, ...
with any exchange functional, e.g., SIC, F30, D30, SK71, B88, G96, ...
and any correlation functional, e.g., MP2, VWN, LYP, ...

and thereby create a well-defined quantum chemical energy procedure. For computational and historical reasons, we may categorize these into four interrelated families (see also Figure 1).

Family	E_T	E_{XC}
1	Orbital functional	Orbital functional
2	Orbital functional	Orbital & density functionals
3	Orbital functional	Density functional
4	Density functional	Density functional

Table 1 E_T, E_X and E_C Energies (Hartrees) of Atoms According to Various Functionals

Functional	H	He	Be	N	Ne	Ar
Kinetic						
H28	+0.500	+2.862	+14.573	+54.401	+128.55	+526.82
TF27	+0.459	+2.561	+13.129	+49.477	+117.77	+489.95
W35	+0.515	+2.879	+14.647	+54.385	+127.84	+524.22
Exchange						
F30	−0.312	−1.025	−2.666	−6.604	−12.099	−30.183
D30	−0.268	−0.883	−2.312	−5.898	−11.026	−27.861
SK71	−0.305	−1.006	−2.580	−6.400	−11.769	−29.292
B88	−0.310	−1.025	−2.657	−6.594	−12.130	−30.152
GGA91	−0.307	−1.016	−2.644	−6.574	−12.107	−30.122
G96	−0.311	−1.028	−2.657	−6.595	−12.136	−30.184
Correlation						
Exact	0	−0.042	−0.094	−0.188	−0.392	-
MP2	0	−0.013	−0.038	−0.049	−0.152	-
Pairs	0	−0.042	−0.084	−0.111	−0.210	−0.378
W38	0	−0.058	−0.110	−0.179	−0.360	−0.661
VWN	−0.022	−0.113	−0.225	−0.429	−0.746	−1.431
LYP	0	−0.044	−0.095	−0.192	−0.383	−0.751
GGA91	−0.007	−0.046	−0.094	−0.192	−0.389	−0.769

We discuss some of the important representatives of each of these four families below.

7.1 Post-Hartree–Fock Theories

Family 1 derives both E_T and E_{XC} from the orbitals. The archetype is Hartree–Fock (HF) theory

$$E^{HF} = E_T^{H28} + E_V + E_J + E_X^{F30} \tag{21}$$

itself, which uses the H28 and F30 orbital functionals. Beyond this lies the wide array of 'post-Hartree–Fock' theories including MP2, MP3, MP4, CCSD, QCISD, full CI, etc. which are beyond the scope of this article but are discussed elsewhere.

7.2 Pure Density Functional Theories

Family 4 derives both E_T and E_{XC} from the density. The archetypes are Thomas–Fermi theory

$$E^{TF} = E_T^{TF27} + E_V + E_J \tag{22}$$

which Parr and Yang call 'an exquisitely simple model'[4] and Thomas–Fermi–Dirac theory

$$E^{TFD} = E_T^{TF27} + E_V + E_J + E_X^{D30} \tag{23}$$

Although very elegant, simple theories like TF and TFD are qualitative models at best. Teller has proven, for example, that TF can never bind a molecule with respect to dissociated atoms. Unfortunately, even the more sophisticated members of this family, such as

$$E^{WBLYP} = E_T^{W35} + E_V + E_J + E_X^{B88} + E_C^{LYP} \tag{24}$$

are not accurate enough to be chemically useful. The key to this problem is that the existing kinetic density functionals yield large absolute errors. It was this realization that eventually led to proposals to introduce the H28 orbital functional into density functional theory.

7.3 Kohn–Sham Density Functional Theories

Although it appears simple in the context of this chapter on SCF, the idea to consider blends of the HF and density functional theories was revolutionary. As Figure 1 shows, it originated with Slater in 1951 who proposed that the Hartree–Fock energy expression (21) be simplified by replacing F30 with D30 to yield

$$E^{HFS} = E_T^{H28} + E_V + E_J + E_X^{D30} \tag{25}$$

which is called Hartree–Fock–Slater theory but whose systematic name is Hartree–Dirac theory. In one sense, it lies half-way between the HF and TFD theories but, for many properties, it works better than either. The reason for its success is not yet clear and remains controversial.

Finding that D30 systematically underestimates F30, Slater also proposed that the last term in (25) be increased by roughly 10%. The resulting semiempirical model is called $X\alpha$ theory and was used widely for many years.

Kohn and Sham later proved that Slater's intuitively motivated suggestion can be justified theoretically and procedures which combine the orbital-based Hartree kinetic functional with density-based exchange-correlation functionals are now called Kohn–Sham density functional theories. They are shown as family 3 in Figure 1.

A particularly popular Kohn–Sham procedure is the local spin density approximation, or LSDA, which is obtained by adding the jellium correlation functional to HFS theory to yield

$$E^{LSDA} = E_T^{H28} + E_V + E_J + E_X^{D30} + E_C^{VWN} \tag{26}$$

Comparing with equation (21), we see that the LSDA procedure may be viewed as a variant of Hartree–Fock theory in which Fock exchange has been replaced by the exchange-correlation energy of jellium. For a variety of chemical properties, it works better than HF or HFS theories but, because VWN overcorrelates, the LSDA tends to overbind. The LSDA is a truly *ab initio* theory that can be rigorously derived from

the Schrödinger equation. It should not be forgotten, however, that this theoretical model of chemistry results from choosing jellium as the reference system. In principle, there is nothing to prevent our choosing an alternative (and, perhaps, more suitable) reference.

Since the 1980s, a wide variety of Kohn–Sham procedures with even better predictive power have been proposed. One of the most popular of these, which uses the B88 and LYP functionals, is the BLYP method

$$E^{\mathrm{BLYP}} = E_{\mathrm{T}}^{\mathrm{H28}} + E_{\mathrm{V}} + E_{\mathrm{J}} + E_{\mathrm{X}}^{\mathrm{B88}} + E_{\mathrm{C}}^{\mathrm{LYP}} \tag{27}$$

Once a number of careful computational studies had demonstrated its usefulness, BLYP was quickly adopted by the quantum chemical community and has subsequently enjoyed widespread use. Typically, it predicts atomization energies, ionization energies, electron affinities and proton affinities of small 'normal' molecules to within roughly 20 kJ mol^{-1} of their exact (i.e., experimental) values. However, it tends to underestimate barrier heights and can fail spectacularly in its prediction of isomerization energies between very dissimilar isomers.

7.4 Hybrid Density Functional Theories

Becke and others have also introduced 'hybrid' or 'adiabatic connection' methods, in which a part of F30 is added to a Kohn–Sham procedure. One of these is the popular B3LYP method

$$\begin{aligned} E^{\mathrm{B3LYP}} = {} & E_{\mathrm{T}}^{\mathrm{H28}} + E_{\mathrm{V}} + E_{\mathrm{J}} + (1-c_1)E_{\mathrm{X}}^{\mathrm{D30}} + c_1 E_{\mathrm{X}}^{\mathrm{F30}} \\ & + c_2 \Delta E_{\mathrm{X}}^{\mathrm{B88}} + (1-c_3)E_{\mathrm{C}}^{\mathrm{VWN}} + c_3 E_{\mathrm{C}}^{\mathrm{LYP}} \end{aligned} \tag{28}$$

where the coefficients c_1, c_2 and c_3 were derived by fitting experimental data. These methods cannot be derived rigorously and, at least in their current incarnations, possess a decidedly empirical flavour. Nonetheless, they are widely embraced and their popularity derives from their ability to predict the atomization energies of small 'normal' systems to within roughly 10 kJ mol^{-1} of their exact values. However, they are still far from perfect and remain the focus of much current research work. They are shown as family 2 in Figure 1.

8 COMPUTATIONAL ASPECTS

8.1 The SCF Procedure

To this point, our discussion has focused exclusively on the energy contributions that arise in an SCF context. However, if we wish to obtain optimized molecular orbitals $\psi_i(\mathbf{r})$, our goal is not just to compute, but to minimize, the energy. The feature shared by all self-consistent field methods is that each electron moves in an average potential due to all of the (other) electrons. Thus, each occupies an orbital $\psi_i(\mathbf{r})$ governed by a Schrödinger equation

$$\mathbf{F}\psi_i = \varepsilon_i \psi_i \tag{29}$$

where $\mathbf{F}$ is called the Fock operator and ε_i is called the orbital energy or orbital eigenvalue. The ideal $\mathbf{F}$ implicitly contains all of the complex physics of electron–electron interactions but, as noted earlier, this ultimate $\mathbf{F}$ is unknown. In HF theory, the Fock operator is given by

$$\mathbf{F}_{\mathrm{HF}} = -\frac{1}{2}\nabla^2 + V(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}\mathbf{r}' + \nu^{\mathrm{F30}} \tag{30}$$

where ν^{F30} is the potential due to the F30 exchange functional. The relationship between equations (3) and (30) should be clear: in HF theory, each electron is assumed to move in a field that is the sum of the Coulomb potential and the F30 potential. The explicit form of ν^{F30}, which is often described as a non-local potential, can be found in Ref. 3.

Kohn–Sham DFT may be seen as a generalization of HF theory in which ν^{F30} is replaced by the potential due to the chosen E_{XC}, i.e.,

$$\mathbf{F}_{\mathrm{KS}} = -\frac{1}{2}\nabla^2 + V(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}\mathbf{r}' + \nu_{\mathrm{XC}}(\mathbf{r}) \tag{31}$$

However, what is the potential ν_{XC} associated with a nominated density functional for E_{XC}? According to the Hohenberg–Kohn–Sham prescription,[2,7] ν_{XC} is the functional derivative of E_{XC} with respect to the density $\rho(\mathbf{r})$, i.e.,

$$\nu_{\mathrm{XC}}(\mathbf{r}) \stackrel{\mathrm{def}}{=} \frac{\delta E_{\mathrm{XC}}(\mathbf{r})}{\delta \rho(\mathbf{r})} \tag{32}$$

The density functionals that we have considered are all of the general form

$$E_{\mathrm{XC}} = \int f(\rho, \rho^x, \rho^y, \rho^z)\,\mathrm{d}\mathbf{r} \tag{33}$$

where $\rho^x = \partial\rho/\partial x$, etc. Standard variational calculus then yields the result

$$\nu_{\mathrm{XC}} = \frac{\partial f}{\partial \rho} - \frac{d}{dx}\frac{\partial f}{\partial \rho^x} - \frac{d}{dy}\frac{\partial f}{\partial \rho^y} - \frac{d}{dz}\frac{\partial f}{\partial \rho^z} \tag{34}$$

and, of course, only the first term of this survives for non-gradient-corrected functionals.

To solve the SCF problem within a basis set $\eta_i(\mathbf{r})$, we need the Fock matrix elements

$$F_{ij}^{\mathrm{XC}} = \langle \eta_i | \nu_{\mathrm{XC}} | \eta_j \rangle = \int \eta_i(\mathbf{r}) \nu_{\mathrm{XC}}(\mathbf{r}) \eta_j(\mathbf{r})\,\mathrm{d}\mathbf{r} \tag{35}$$

to set up the secular equations. We then solve these equations to find new MO coefficients, use these to construct a new density, and iterate this process until convergence is achieved.

8.2 The Coulomb Problem

Thus far, we have said little about the calculation of the Coulombic energies E_{V} and E_{J} defined in equations (12) and (13). However, they should not be overlooked for it is found in practice that, for medium and large molecules, E_{J} is the most expensive term in equation (5). This may seem surprising, given that equation (13) appears to be relatively simple, and raises the important issue of computational scaling.

Suppose that we wish to calculate the electronic energy of a large chemical system. The evaluation of the Hartree kinetic functional and most of the functionals in Sections 4 and 5 involves only a complicated integration over all space. In contrast, the evaluation of

$$E_{\mathrm{J}} = \frac{1}{2}\sum_i^n \sum_j^n \int\int \frac{\psi_i^2(\mathbf{x}_1)\psi_j^2(\mathbf{x}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\,\mathrm{d}\mathbf{x}_1\,\mathrm{d}\mathbf{x}_2 \tag{36}$$

involves a double sum of integrals over all space. Physically, the double sum reminds us that E_J involves all pairs of orbitals and also suggests that the cost of its computation is $O(n^2)$, i.e., it scales quadratically with n. Thus, if we double the size of our molecule, E_J will involve four times as many interactions and, judging by (36), will take four times as long to calculate. If the orbitals ψ_i are built from Gaussian basis functions, the double integrals are not hard[32] but $O(n^2)$ of them are needed. This is the heart of the Coulomb problem.

For many years, finding an efficient passage through 'the integral bottleneck' was one of the major concerns of quantum chemists. Indeed, until the advances by Pople et al. in the late 1960s, this was the single greatest obstacle impeding the progress of the field. Fortunately, the approaches to molecular integrals have continued to improve ever since that time and very efficient algorithms with highly tuned computer implementations now exist. Nevertheless, although such techniques work well for small systems, their costs still scale quadratically and, for larger systems, rise impractically quickly.

It was realized long ago that the Coulomb interactions between distant parts of a system need not necessarily be treated in the same way as those between adjacent parts. However, it was not clear how to use this fact to enhance the efficiency of Coulomb algorithms. In 1987, Greengard and Rokhlin invented the Fast Multipole Method,[33] an ingenious algorithm for computing E_J in only $O(n)$ work by partitioning the six-dimensional integration space into a 'well-separated' and a 'not well-separated' region. The latter is handled in the usual way but the former (which is much larger) is integrated by manipulation of the multipole expansion

$$\frac{1}{r_{12}} = \frac{1}{r_1}\sum_{k=0}^{\infty}\left(\frac{r_2}{r_1}\right)^k P_k\left(\frac{\mathbf{r}_1\cdot\mathbf{r}_2}{r_1 r_2}\right) \tag{37}$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. Originally, the FMM could be applied only if the ψ_i^2 were point charges but, later, the method was generalized to treat arbitrary localized charge distributions.[34]

The FMM was the original member of the family of 'linear methods' or '$O(n)$ methods' for solving the Coulomb problem. Once it had been discovered that such algorithms exist, it was clear that one should try to determine the most efficient of the $O(n)$ methods and there has been a considerable research effort along these lines. The answer, however, is not yet known.

In the KWIK algorithm,[35] the Coulomb function itself is partitioned by the identity

$$\frac{1}{r_{12}} \equiv \frac{f(r_{12})}{r_{12}} + \frac{1 - f(r_{12})}{r_{12}} \tag{38}$$

where the function f decays rapidly and $f(0) = 1$. This splits $1/r$ into a singular short-range function and a non-singular long-range function and thus breaks E_J into a short-range part and a long-range part. The short-range energy involves only neighboring charge distributions; the long-range energy can be found using Fourier transforms or related techniques. It has been shown that the 'optimal' separator function $f(r)$ is a Parabolic Cylinder function.

8.3 The Grid Problem

Evaluation of most of the functionals in Sections 4 and 5 leads to integrals of the form

$$E = \int f(\rho(\mathbf{r}), x(\mathbf{r}))\,\mathrm{d}\mathbf{r} \tag{39}$$

In certain very special cases, such integrals can be found in closed form. However, in general, the integrand is so complicated that the integrals have to be computed approximately using quadrature on a three-dimensional grid of N_{grid} points placed in and around the system, i.e.,

$$E \approx \sum_{i=1}^{N_{\text{grid}}} w_i f(\rho(\mathbf{r}_i), x(\mathbf{r}_i)) \tag{40}$$

This is one of the least attractive features of current DFT theories and we note that it does not arise in HF theory because both the H28 and F30 functionals can be evaluated in closed form.

Much work has been done on the construction of efficient grids for such calculations and the recent contributions of Becke, Handy, te Velde, Treutler and Knowles[36] are noteworthy. Most modern grids follow Becke's suggestion to partition the difficult molecular integral in equation (39) into a sum of atomic integrals using a 'fuzzy' Voronoi decomposition.[37] Each atomic integral is then evaluated by introducing a local spherical polar system centered on the nucleus and using quadrature rules to integrate the radial and angular variables. A wide variety of quadrature schemes have been proposed.

For the same reasons that it was beneficial to introduce 'standard basis sets' (e.g., STO-3G, cc-pVTZ, etc.) into quantum chemistry, it is also valuable to employ 'standard grids' in DFT. The SG-1 grid[38] was one of the first of these to be introduced and is constructed as follows:

Radial quadrature is accomplished by an N-point Handy–Euler–Maclaurin rule with $N = 50$, i.e.,

$$\int_0^{\infty} r^2 G(r)\,\mathrm{d}r \approx \sum_{k=1}^{N} a_k G(r_k) \tag{41}$$

$$a_k = \frac{2k^5 R^3 (N+1)}{(N+1-k)^7} \qquad r_k = \frac{k^2 R}{(N+1-k)^2} \tag{42}$$

where R is the appropriate Slater atomic radius. The first ten such radii are:

Nucleus	H	He	Li	Be	B
R (Bohr)	1.0000	0.5882	3.0769	2.0513	1.5385

Nucleus	C	N	O	F	Ne
R (Bohr)	1.2308	1.0256	0.8791	0.7692	0.6838

Angular quadrature is accomplished by an M-point Lebedev rule where $M = 6$, 38, 86 or 194.

Relatively few angular points (e.g., 6) are used in the core region (i.e., where $r_k \ll R$).

Relatively many angular points (e.g., 194) are used in valence regions (i.e., where $r_k \approx R$).

By construction, Lebedev quadrature rules exactly integrate all spherical harmonics up to a certain degree on the surface of a sphere. The 6, 38, 86 and 194 point rules are exact for all spherical harmonics up to 3rd, 9th, 15th and 23rd degree, respectively.

Typically, each atom supports about 2500 grid points and the SG-1 grid introduces errors of roughly 0.1 kJ mol^{-1} per atom in the system. Although errors of this magnitude are tolerable for some purposes, it is frequently desirable to use larger, more accurate, grids.

9 DERIVATION OF THE THOMAS–FERMI KINETIC FUNCTIONAL

Most density functionals derive from arguments that are complicated, dubious or both. The elegant derivation of TF27 is an exception, however, and is worthy of close examination. Consider a cube with sidelength L and volume V and place the origin at one corner of the cube. The Schrödinger equation for the state $\mathbf{m}$ of a single electron confined within the cube is

$$-\frac{1}{2}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi = \varepsilon\psi \tag{43}$$

and the wavefunction and energy of state $\mathbf{m} = (m_x, m_y, m_z)$ are therefore given by

$$\psi_{\mathbf{m}} = \sin\left(\frac{\pi m_x x}{L}\right)\sin\left(\frac{\pi m_y y}{L}\right)\sin\left(\frac{\pi m_z z}{L}\right) \tag{44}$$

$$\varepsilon_{\mathbf{m}} = \frac{\pi^2 m^2}{2L^2} \qquad (m^2 = m_x^2 + m_y^2 + m_z^2) \tag{45}$$

These states can be depicted diagrammatically as lattice points in (m_x, m_y, m_z) space. Thus, the number of states with energy less than $\varepsilon_{\mathbf{m}}$ is given approximately by the volume of an octant of a sphere of radius m. If we place n non-interacting alpha electrons into the cube, they will fill the lowest n states and $m_{\max}$, the largest occupied m value, will therefore satisfy

$$n \approx \frac{1}{8}\left(\frac{4\pi m_{\max}^3}{3}\right) \quad \Leftrightarrow \quad m_{\max} \approx \left(\frac{6n}{\pi}\right)^{1/3} \tag{46}$$

The total energy of non-interacting electrons is given by the sum of their individual energies and, obviously, this energy is entirely kinetic. Thus, the total kinetic energy is

$$E_{\mathrm{T}} = \sum_{|\mathbf{m}|\le m_{\max}} \varepsilon_{\mathbf{m}} \tag{47}$$

This can be approximated by an integral over an octant of a sphere of radius $m_{\max}$, i.e.,

$$E_{\mathrm{T}} \approx \frac{1}{8}\int_0^{m_{\max}} 4\pi m^2 \left(\frac{\pi^2 m^2}{2L^2}\right) \mathrm{d}m$$

$$= \frac{\pi^3 m_{\max}^5}{20L^2} = \frac{3}{10}(6\pi^2)^{2/3}\left(\frac{n}{L^3}\right)^{5/3} L^3 \tag{48}$$

and, in terms of the mean alpha density $\rho_\alpha = n/V$, this becomes

$$E_{\mathrm{T}} \approx \frac{3}{10}(6\pi^2)^{2/3}\rho_\alpha^{5/3} V \tag{49}$$

Finally, we make the local density approximation, i.e., suppose that this formula is valid in an infinitesimal volume $\mathrm{d}V$ and then integrate over all such volume elements to obtain

$$E_{\mathrm{T}} = \frac{3}{10}(6\pi^2)^{2/3}\int \rho_\alpha^{5/3}(\mathbf{r})\,\mathrm{d}\mathbf{r} \tag{50}$$

It is unfortunate that this beautiful functional is not accurate enough to be chemically useful and is therefore rarely used.

10 RELATED ARTICLES

Basis Sets: Correlation Consistent Sets; Configuration Interaction; Coupled-cluster Theory; Density Functional Applications; Density Functional Theory Applications to Transition Metal Problems; G2 Theory; Integrals of Electron Repulsion; Integrals: Overlap; Linear Scaling Methods for Electronic Structure Calculations; Localized MO SCF Methods; Møller–Plesset Perturbation Theory; Monte Carlo Quantum Methods for Electronic Structure; Numerical Hartree–Fock Methods for Molecules; Pseudospectral Methods in Ab Initio Quantum Chemistry; Self-consistent Reaction Field Methods; Symmetry in Hartree–Fock Theory.

11 REFERENCES

1. E. Schrödinger, *Ann. Physik*, 1926, **79**, 361–376.
2. P. Hohenberg and W. Kohn, *Phys. Rev. B*, 1964, **136**, 864–871.
3. A. Szabo and N. S. Ostlund, 'Modern Quantum Chemistry', Macmillan, New York, 1982.
4. R. G. Parr and W. Yang, 'Density-Functional Theory of Atoms and Molecules', Oxford University Press, Oxford, 1989.
5. R. M. Dreizler and E. K. U. Gross, 'Density Functional Theory', Springer-Verlag, Berlin, 1990.
6. J. C. Slater, *Phys. Rev.*, 1951, **81**, 385–390.
7. W. Kohn and L. J. Sham, *Phys. Rev. A*, 1965, **140**, 1133–1138.
8. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372–1377.
9. D. R. Hartree, *Proc. Camb. Phil. Soc.*, 1928, **24**, 89–110.
10. V. Fock, *Z. Physik*, 1930, **61**, 126–148.
11. L. H. Thomas, *Proc. Camb. Phil. Soc.*, 1927, **23**, 542–548.
12. E. Fermi, *Rend. Accad. Lincei*, 1927, **6**, 602–607.
13. P. A. M. Dirac, *Proc. Camb. Phil. Soc.*, 1930, **26**, 376–385.
14. D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.*, 1980, **45**, 566–569.
15. S. J. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200–1211.
16. E. Wigner, *Trans. Faraday Soc.*, 1938, **34**, 678–685.
17. P. A. Stewart and P. M. W. Gill, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 4337–4341.
18. C. F. von Weizsacker, *Z. Physik*, 1935, **96**, 431–458.
19. C. H. Hodges, *Can. J. Phys.*, 1973, **51**, 1428–1437.
20. D. R. Murphy, *Phys. Rev. A*, 1981, **24**, 1682–1688.
21. L. J. Sham, in 'Computational Methods in Band Theory', ed. P. J. Marcus, J. F. Janak, and A. R. Williams, Plenum, New York, 1971.
22. L. Kleinman and S. Lee, *Phys. Rev. B*, 1988, **37**, 4634–4636.
23. F. Herman, J. P. van Dyke, and I. B. Ortenburger, *Phys. Rev. Lett.*, 1969, **32**, 807–811.
24. A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098–3100.
25. P. M. W. Gill, *Mol. Phys.*, 1996, **89**, 433–445.
26. C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.
27. R. Colle and O. Salvetti, *Theor. Chim. Acta*, 1975, **37**, 329–334.
28. B. Miehlich, A. Savin, H. Stoll, and H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200–206.
29. M. Levy, 'Single-Particle Density in Physics and Chemistry', ed. N. H. March and B. M. Deb, Academic, London, 1987.
30. J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B*, 1992, **46**, 6671–6687.
31. E. R. Davidson, S. A. Hagstrom, S. J. Chakravorty, V. M. Umar, and C. Froese Fischer, *Phys. Rev. A*, 1991, **44**, 7071–7083.

32. P. M. W. Gill, *Adv. Quantum Chem.*, 1994, **25**, 141-205.
33. L. Greengard and V. Rokhlin, *J. Comput. Phys.*, 1987, **73**, 325-348.
34. C. A. White, B. G. Johnson, P. M. W. Gill, and M. Head-Gordon, *Chem. Phys. Lett.*, 1994, **230**, 8-16.
35. J. P. Dombroski, S. W. Taylor, and P. M. W. Gill, *J. Phys. Chem.*, 1996, **100**, 6272-6276.
36. M. E. Mura and P. J. Knowles, *J. Chem. Phys.*, 1996, **104**, 9848-9858.
37. A. D. Becke, *J. Chem. Phys.*, 1988, **88**, 2547-2553.
38. P. M. W. Gill, B. G. Johnson, and J. A. Pople, *Chem. Phys. Lett.*, 1993, **209**, 506-512.

Density Functional Theory Applications to Transition Metal Problems

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Abbreviations

B3LYP = Becke's 3-parameter hybrid functional using the nonlocal correlation functional due to Lee, Yang, and Parr; BP = nonlocal exchange correlation functional due to Becke and Perdew; DF = Dirac-Fock; DIIS = direct inversion of iterative subspace; KS = Kohn-Sham; LDA = local density approximation; LSDA = local spin density approximation; (R)ECP = (relativistic) effective core potential; TM = transition metal.

1 INTRODUCTION

The past two decades have witnessed an ever growing interest of experimentalists and theoreticians alike in molecules and ions containing transition metal (TM) atoms. The reasons for this are obvious, since TM atoms are found ubiquitously in many important areas of chemistry. Among the most prominent fields dominated by interactions involving TMs are the following. The combination of TMs with organic reagents has created a whole, well matured field, i.e., organometallic chemistry. TM-containing molecules also play a crucial role in many aspects of biochemistry and are very often responsible for the specific functionality of a particular biomolecule. TM clusters mediate catalytic surface processes in many reactions. And, last but certainly not least, TMs are the active sites in almost all molecules relevant in catalytic processes and are thus one of the cornerstones in this highly significant field of present research.

The characters, or equivalently, the electronic structures of TM compounds relevant in these areas are just as diverse. They range from electronically saturated, closed shell TM complexes, where the metal is usually surrounded by enough ligands so that the 18-electron rule is obeyed, up to species with many unpaired electrons, giving rise to a plethora of possible electronic states. Indeed, much of the activity displayed by TM compounds is due to this flexibility in the electronic structure (i.e., varying occupation) of the nd, $(n + 1)$s and, to some extent, $(n + 1)$p shells of the central metal atom, characterized by unpaired and hence chemically very important electrons. Intimately interwoven with this diversity of electronic scenarios available for the various 'flavors' of TM compounds are the difficulties of finding a quantum chemical strategy with a satisfactory 'price/performance ratio', i.e., one that can provide meaningful results with acceptable computational effort. Difficulties arise already when closed shell TM compounds are to be described (see ***Transition Metal Chemistry***).[1] The real challenge, however, is met in open shell species. The mixing of the large number of low-lying atomic electronic states derived from different occupations of the valence nd and $(n + 1)$s orbitals to achieve the optimal bonding together with the relative sizes of the valence s and d orbitals leads to large differential (dynamic and static) correlation effects (see *Electron Correlation*) which are very difficult to account for. Efficient standard MO-based schemes, such as second-order perturbation theory (MP2), usually fail, as pointed out rather clearly by Taylor: 'Transition metal chemistry, in particular, is a graveyard for UHF-based MP methods'.[2] One possible way out is to use very sophisticated and demanding correlated methods such as multi-reference configuration interaction and variants thereof. Unfortunately, this brute force approach is inevitably limited to small systems by computing resources and cannot be applied routinely to molecules containing more than two or three heavy atoms[3] (see ***Transition Metals: Applications***).

However, there is one class of methods which has recently gained substantial impact in the study of closed and open shell TM compounds, viz. schemes based on approximate density functional theory (DFT). For example, even very simple forms of DFT give a surprisingly good qualitative description of the notoriously difficult Cr_2 $^1\Sigma_g^+$ ground state potential.[4] This contribution will focus on the scope and the limitations of the burgeoning field of DFT applications to TM problems and is organized as follows. First, we will highlight very briefly some of the central theoretical aspects of DFT and give an explanation why this approach has matured in only a few years from an exotic method used almost exclusively by solid state physicists to a valuable player in the computational chemistry arena, and why it has proven so useful for the investigation of TM compounds in particular. In this context, we will also discuss some of the conceptual weaknesses of DFT and how to cope with them. The main body of this article will, however, be devoted to demonstrating the value of DFT-based methods for investigating TM compounds chiefly against the background of organometallic chemistry. We will review examples of DFT calculations for obtaining atomic excitation