Chapter 3

The Pair Density in Approximate Density Functionals: The Hidden Agent

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1. INTRODUCTION

In this chapter, we review the connection between density functional methods [1] and wavefunction methods [2]. Simple models of the pair density are shown to lead naturally to the local density approximation for exchange and correlation. The rigorous basis for this approach is exact density functional theory [1, 3-7]. We review recent advances from a pair density perspective.

2. MODELLING (OR MUDDLING?) THE PAIR DENSITY

Of crucial importance in many problems in chemistry is determining the electronic structure of the system of interest. Much research has been directed towards finding the electronic ground state, which features in a wide range of calculations: from determining static properties such as molecular bond lengths and angles, to dynamical properties such as rates of reaction within a Born-Oppenheimer approach. In particular, the ground state energy as a function of nuclear coordinates is important. Solving the many-electron Schrödinger equation for the ground state is equivalent to the variational problem of minimizing the energy over all antisymmetric normalized wavefunctions. The energy has three components; in atomic units ($\hbar = e^2 = m = 1$) the Schrödinger equation for N electrons is

$$\hat{H}\Psi(x_1...x_N) = \left(\hat{T} + \hat{V}_{ext} + \hat{V}_{ee}\right)\Psi(x_1...x_N)$$
$$= \left(-\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i=1}^{N} v_{ext}(\mathbf{r}_i) + \frac{1}{2}\sum_{j\neq i}^{N}\sum_{i=1}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right)\Psi(x_1...x_N)\,, \quad (2.1)$$

where $\hat{T}, \hat{V}_{ext}$, and $\hat{V}_{ee}$ are the kinetic energy, external potential (*e.g.* electron-nuclear attraction), and electron-electron repulsion operators respectively. We use $\mathbf{x}$ to denote the spatial and spin variables, $\mathbf{x} = (\mathbf{r}, \sigma)$. Only the one- and two- particle density matrices appear in the energy:

$$E = -\frac{1}{2}\int d\mathbf{r}\nabla_{\mathbf{r}}^2\Gamma_1(\mathbf{r}';\mathbf{r})|_{\mathbf{r}'=\mathbf{r}} + \int d\mathbf{r} v_{ext}(\mathbf{r})\rho_1(\mathbf{r}) + \int d\mathbf{r}'\int d\mathbf{r}\frac{\rho_2(\mathbf{r}',\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\,, \quad (2.2)$$

where

$$\Gamma_1(\mathbf{r}';\mathbf{r}) = N\sum_{\sigma_1...\sigma_N}\int d\mathbf{r}_2...d\mathbf{r}_N\Psi^*(\mathbf{r}'\sigma_1, x_2...x_N)\Psi(\mathbf{r}\sigma_1, x_2...x_N) \quad (2.3)$$

is the spin-less one-particle reduced density matrix;

$$\rho_2(\mathbf{r}',\mathbf{r}) = \frac{N(N-1)}{2}\sum_{\sigma_1...\sigma_N}\int d\mathbf{r}_3...d\mathbf{r}_N|\Psi(\mathbf{r}\sigma_1, \mathbf{r}'\sigma_2, x_3...x_N)|^2 \quad (2.4)$$

is the spin-less reduced pair density; and the (one-particle) density is

$$\rho_1(\mathbf{r}) = \Gamma_1(\mathbf{r};\mathbf{r}) = \frac{2}{N-1}\int d\mathbf{r}'\rho_2(\mathbf{r}',\mathbf{r})\,. \quad (2.5)$$

The pair density has the physical interpretation that $\rho_2(\mathbf{r},\mathbf{r}')d\mathbf{r}d\mathbf{r}'$ is half the joint probability of finding an electron in volume $d\mathbf{r}'$ around $\mathbf{r}'$ and one in a volume $d\mathbf{r}$ around $\mathbf{r}$. If the electrons were independent, ρ_2 would just be half the product of the one-particle densities $\rho_1(\mathbf{r})\rho_1(\mathbf{r}')/2$. It is then intuitive to define the exchange-correlation potential hole ρ_{XC} through

$$\rho_2(\mathbf{r}',\mathbf{r}) = \rho_1(\mathbf{r})\left(\rho_1(\mathbf{r}') + \rho_{XC}(\mathbf{r}',\mathbf{r})\right)/2\,. \quad (2.6)$$

Given that there is an electron at $\mathbf{r}$, $\rho_{XC}(\mathbf{r}',\mathbf{r})$ gives the difference between the true average density of electrons at $\mathbf{r}'$ and that density if the electrons were independent. In this sense, a non-zero ρ_{XC} is due to exchange and correlation effects. Substituting this decomposition of the pair density into the interaction energy expectation value, we get

$$V_{ee} = U + U_{XC}\,, \quad (2.7)$$

where

$$\mathrm{U} = \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{\rho_1(\mathbf{r})\rho_1(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{2.8}$$

is the Hartree energy and

$$\mathrm{U}_{\mathrm{XC}} = \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{\rho_1(\mathbf{r})\rho_{\mathrm{XC}}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{2.9}$$

is the exchange-correlation potential energy.

Equations (2.2) - (2.4) hold out the hope that, with knowledge of only the above one- and two-point functions, we can find the ground-state energy by searching over all possible combinations and finding the lowest value. Unfortunately, this hope is over-optimistic, as we must still determine which such functions arise from a physically allowable wavefunction. For example, appropriate one- and two-particle density matrices must have appropriate normalizations and symmetry properties related to the underlying wavefunction. This is a central difficulty in using the one- and two-matrices in a calculation and is treated in other chapters in this book.

Suppose, instead of calculating a full wavefunction, we give up the variational principle and choose to make a model for the pair density in terms of simpler quantities. How much can we glean about the pair density from fundamental properties such as these? Is it enough to make a plausible model for it for typical systems without ever calculating the full wavefunctions? Rather, less ambitiously and more realistically, with a view to estimating only the interaction energy U_{XC} we need only a model for the spherical average of the hole ρ_{XC} [8], as defined by

$$\rho_{\mathrm{XC}}^{\mathrm{sph}}(\mathbf{r},\mathrm{u}) = \int \frac{d\Omega_{\mathbf{u}}}{4\pi}\rho_{\mathrm{XC}}(\mathbf{r},\mathbf{r}+\mathbf{u})\,. \tag{2.10}$$

Then

$$\mathrm{U}_{\mathrm{XC}} = 2\pi\int d\mathbf{r}\rho_1(\mathbf{r})\int_0^{\infty} d\mathrm{u}\mathrm{u}\rho_{\mathrm{XC}}^{\mathrm{sph}}(\mathbf{r},\mathrm{u})\,. \tag{2.11}$$

First let us consider the simpler problem of exchange. That is, we shall consider the generic non-degenerate case of a wavefunction that is a single Slater determinant of occupied orbitals. In figures 3.1 and 3.2 we plot the exact spherically averaged exchange holes for the hydrogen atom and for the spin-unpolarized uniform electron gas. These two cases are in a sense at opposite ends of the spectrum of systems of typical interest in atomic and molecular and chemical physics: the hydrogen atom with one electron being the smallest, having an exponentially decaying wavefunction and the uniform electron gas with an

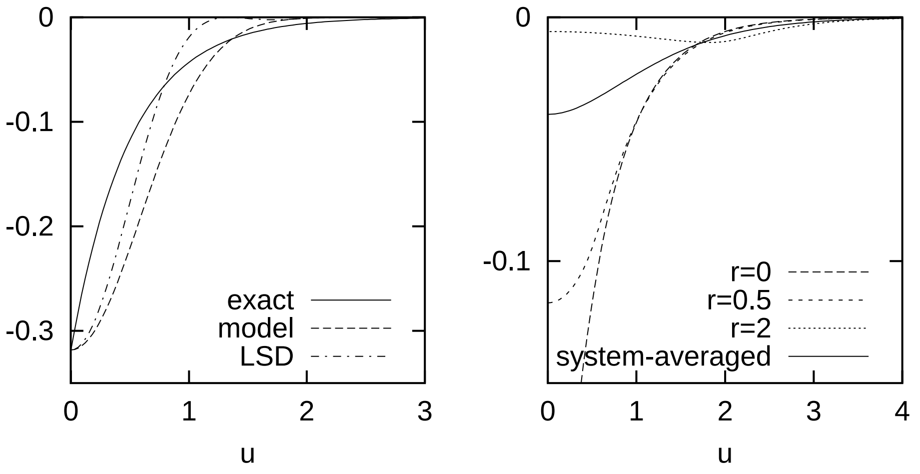

Figure 3.1 Spherically-averaged exchange hole for hydrogen, $\rho_{\mathrm{X}}^{\mathrm{sph}}(\mathbf{r},\mathrm{u})$, as a function of separation u. The left figure shows the exact hole and two approximations at the nucleus $\mathbf{r}=0$. The right figure shows the exact hole at various positions $\mathbf{r}$ indicated, as well as a system-average, $\int \mathrm{d}\mathbf{r}\rho_1(\mathbf{r})\rho_{\mathrm{X}}^{\mathrm{sph}}(\mathbf{r},\mathrm{u})$.

infinite number of electrons having plane-wave orbitals. Yet their spherically averaged exchange holes have a remarkably similar shape, except (i) when **r** is too far away from the nucleus in the case of H, and (ii) in the tails of the uniform gas hole where there are small oscillations underneath a decaying envelope. (The first oscillation is beyond the range plotted in the figure). Because the electron density decays exponentially away from the nucleus of the H-atom, the regions further out from the nucleus are exponentially less heavily weighted in any energy calculation (see Eq. (2.11)). Also the tails of the exchange hole, where there are modulations in the exchange hole density for the uniform gas, contribute significantly less due to the reduced amplitude there.

We now attempt to model this generic behavior of the spherically averaged exchange hole considering only fundamental properties of the underlying wavefunction. We arbitrarily choose a simple gaussian shape as a function of u:

$$\rho_{\mathrm{X}}^{\mathrm{sph,mod}}(\mathbf{r},\mathrm{u}) = -\mathrm{A}(\mathbf{r})\mathrm{e}^{-\mathrm{a}(\mathbf{r})\mathrm{u}^2}\,. \tag{2.12}$$

Properties of a wavefunction-derivable pair density are naturally expressed in terms of the exchange-correlation hole, or, in the exchange case, the exchange hole. Normalization of the wavefunction translates into a normalization condition for the pair density which becomes a

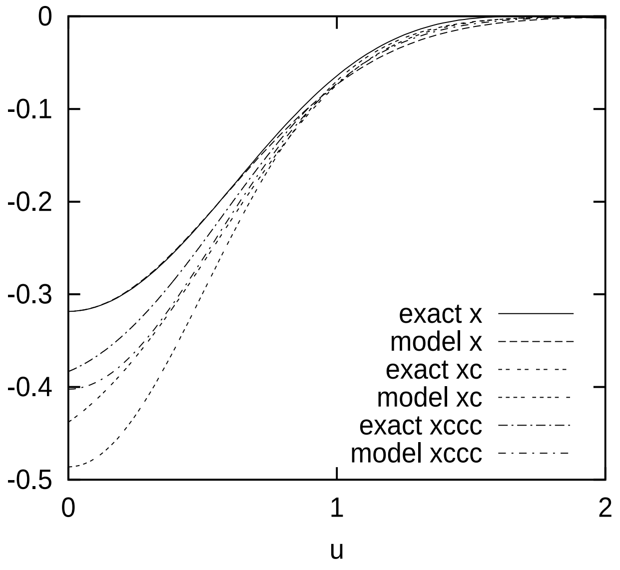

Figure 3.2 Spherically-averaged holes for the unpolarized uniform electron gas at density $\rho_1 = 2/\pi \approx 0.6366$, as a function of separation u. Those labelled x are the exchange holes (for the exact case and for our model), xc denotes the exchange-correlation hole and xccc denotes the coupling-constant averaged exchange-correlation hole. The programs for the exact calculations are on the web-site http://www.crab.rutgers.edu/~kieron.

sum-rule for the hole:

$$\int d\mathbf{r} d\mathbf{r}' \rho_2(\mathbf{r},\mathbf{r}') = \frac{N(N-1)}{2} \longrightarrow \int d\mathbf{r} \rho_X(\mathbf{r},\mathbf{r}') = -1 \,. \tag{2.13}$$

(The density is normalized as $\int d\mathbf{r}\rho_1(\mathbf{r}) = N$). This expresses the deficit of the density everywhere else in the system if one electron is found at $\mathbf{r}$. Imposing condition Eq. (2.13) on our model Eq. (2.12) implies:

$$a(\mathbf{r}) = \pi(A(\mathbf{r}))^{2/3} \,. \tag{2.14}$$

Positivity of the pair density translates into the condition

$$\rho_X(\mathbf{r},\mathbf{r}') \geq -\rho_1(\mathbf{r}') \,, \tag{2.15}$$

expressing that the hole cannot be dug deeper than the density itself. We can get an upper bound on $\rho_X(\mathbf{r},\mathbf{r}')$ in the case of exchange: when the wavefunction is a single Slater determinant composed of orbitals ϕ_i, [6]

$$\rho_X(\mathbf{r},\mathbf{r}') = -\frac{|\Gamma_1(\mathbf{r}',\mathbf{r})|^2}{\rho_1(\mathbf{r})} \leq 0 \,, \tag{2.16}$$

where $\Gamma_1(\mathbf{r}', \mathbf{r}) = \sum_{\mathrm{i\ occ.}} \phi_{\mathrm{i}}^*(\mathbf{r}')\phi_{\mathrm{i}}(\mathbf{r})$. For our model, $\mathrm{A}(\mathbf{r}) > 0$ means the inequality in Eq. (2.16) is satisfied everywhere. In fact we can identify $\mathrm{A}(\mathbf{r})$ completely by considering the "ontop" exchange hole: from Eq. (2.16)

$$\rho_{\mathrm{X}}^{\mathrm{sph,mod}}(\mathbf{r}, \mathrm{u} = 0) = -\frac{\rho_{1\uparrow}^2(\mathbf{r}) + \rho_{1\downarrow}^2(\mathbf{r})}{\rho_1(\mathbf{r})} = -\mathrm{A}(\mathbf{r})\,, \tag{2.17}$$

where $\rho_{1\uparrow}(\mathbf{r})$ and $\rho_{1\downarrow}(\mathbf{r})$ are the densities for spin-up and spin-down electrons respectively at point $\mathbf{r}$. Thus our model for the spherically averaged exchange hole involves only the spin densities:

$$\rho_{\mathrm{X}}^{\mathrm{sph,mod}}(\mathbf{r}, \mathrm{u}) = -\mathrm{A}(\mathbf{r})\mathrm{e}^{-\pi \mathrm{A}^{2/3}(\mathbf{r})\mathrm{u}^2} \text{ where } \mathrm{A}(\mathbf{r}) = \frac{\rho_{1\uparrow}^2(\mathbf{r}) + \rho_{1\downarrow}^2(\mathbf{r})}{\rho_1(\mathbf{r})}\,. \tag{2.18}$$

In the fully polarized limit, for example for the hydrogen atom, we have

$$\rho_{\mathrm{X}}^{\mathrm{sph,mod}}(\mathbf{r}, \mathrm{u}) = -\rho_1(\mathbf{r})\mathrm{e}^{-\pi \rho_1^{2/3}(\mathbf{r})\mathrm{u}^2}\,. \tag{2.19}$$

In the unpolarized limit, for example for the unpolarized uniform electron gas,

$$\rho_{\mathrm{X}}^{\mathrm{sph,mod}}(\mathbf{r}, \mathrm{u}) = -\rho_1(\mathbf{r})\mathrm{e}^{-\pi(\rho_1(\mathbf{r})/2)^{2/3}\mathrm{u}^2}/2\,. \tag{2.20}$$

We considered above just some statements about the pair density and its exchange hole arising from the fundamental properties of the underlying physical wavefunction. Yet these, together with a rough guess for the form of the exchange hole motivated by two extreme examples, were enough to make a model for the spherically averaged exchange hole. This model is crude and does not capture all the details of the spherically averaged exchange hole. For example, the exact hole in hydrogen deviates from a gaussian form as $\mathbf{r}$ moves away from the nucleus, while the hole of the uniform gas displays oscillations in its tail. But for the purpose of finding the exchange energy, the crude model is not a bad one. Our model turns out to depend only on the local spin densities and, consequently, the model exchange energy is a *local spin density functional.* Because of constraints on the pair density, a local density approximation should be of moderate accuracy; that is, electronic structure is "short-sighted" [9]. For example, in the spin-unpolarized case, using Eq. (2.20) in Eq. (2.11),

$$\begin{aligned} \mathrm{U}_{\mathrm{X}}^{\mathrm{mod}} &= \frac{1}{2}\int \mathrm{d}\mathbf{r}\rho_1(\mathbf{r}) \int \mathrm{d}\mathbf{r}' \frac{\rho_{\mathrm{X}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &= -\left(\frac{1}{2}\right)^{1/3} \int \mathrm{d}\mathbf{r}\rho_1^{4/3}(\mathbf{r}) \approx -0.794 \int \mathrm{d}\mathbf{r}\rho_1^{4/3}(\mathbf{r})\,. \end{aligned} \tag{2.21}$$

	U_X	U_X^{mod}	U_X^{LDA}	U_{XC}	U_{XC}^{mod}	U_{XC}^{LDA}
He	-1.025	-0.950	-0.88335	-1.103	-1.202	-1.064
Be	-2.674	-2.495	-2.321	-2.843	-3.000	-2.685
Ne	-12.085	-11.848	-11.021	-12.806	-13.109	-12.258

Table 3.1 Exchange and exchange-correlation potential energies for the first three noble gas atoms, calculated exactly, in our model, and by LDA.

This gives a very simple formula for a reasonable estimate of the exchange energy. There is no need to know all the individual orbitals as would be required in the exact calculation (the Hartree-Fock integral):

$$\mathrm{U_X} = -\frac{1}{2}\sum_{\sigma}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{|\sum_{\alpha\,\mathrm{occ.}} \phi^*_{\alpha,\sigma}(\mathbf{r}')\phi_{\alpha,\sigma}(\mathbf{r})|^2}{|\mathbf{r}'-\mathbf{r}|}\,, \tag{2.22}$$

where the sum goes over all occupied orbitals.

These arguments show that, simply because of constraints on the exact pair density, and the fact that the ontop hole depends only on the (spin) density at a point, a reasonably-shaped model for the spherically averaged exchange-correlation hole around that point, should yield results of moderate accuracy. More importantly, this approximation should be extremely *reliable*, as its derivation depends only on features common to *all* electronic systems. Indeed, consider the first two columns of table 3.1 which contain the exchange energy of the first three noble gas atoms, calculated exactly and by our model. Our model gives a good estimate of the exact exchange energy with errors from 7% underestimate for He to 2% underestimate for Ne.

Correlation can be handled in a very similar fashion. Both Eqs. (2.13) and (2.15) are true also for the full exchange-correlation hole $\rho_{\mathrm{XC}} = \rho_{\mathrm{X}} + \rho_{\mathrm{C}}$ for an interacting system; in particular, we have the correlation sum-rule and exchange-correlation sum-rules:

$$\int \mathrm{d}\mathbf{r}\rho_{\mathrm{C}}(\mathbf{r},\mathbf{r}') = 0 \tag{2.23}$$

and

$$\int \mathrm{d}\mathbf{r}\rho_{\mathrm{XC}}(\mathbf{r},\mathbf{r}') = -1\,. \tag{2.24}$$

Given the success of a simple gaussian model for the exchange case, we try a gaussian also for $\rho_{\mathrm{XC}}^{\mathrm{sph}}$. Writing $\rho_{\mathrm{XC}}^{\mathrm{sph,mod}} = -\mathrm{B}(\mathbf{r})\mathrm{e}^{-\mathrm{b}(\mathbf{r})\mathrm{u}^2}$ and using Eq. (2.24), we find $\mathrm{b}(\mathbf{r}) = \pi\mathrm{B}^{2/3}(\mathbf{r})$. Unlike the exchange case we do not have an exact expression for the ontop exchange-correlation hole since it is not so easy to find the form of the wavefunction for interacting systems as it is for the non-interacting case. We look instead towards the uniform electron gas to provide an approximation for the ontop hole for our model, which is very accurate due to the local nature of the ontop hole [10]. The ontop pair density at any point in the system is largely determined by the density at that point. (Indeed, the ontop uniform gas hole was believed to be exact for many years [11] and only recently proved not to be quite exact except in the exchange limit, fully-spin polarized limit and low-density limit [12]). The exchange-correlation hole of the uniform gas has been accurately parametrized [13]; we consider here the high-density limit only. This gives the first order correction to the exchange hole due to correlation [14]. We have [10] for the spin-unpolarized case,

$$\mathrm{B}(\mathbf{r}) = \rho_{\mathrm{XC}}^{\mathrm{sph}}(\mathbf{r}, \mathrm{u}=0) \approx \rho_1(\mathbf{r})(1+\alpha \mathrm{r_s}(\mathbf{r}))/2\,, \tag{2.25}$$

where $\mathrm{r_s}(\mathbf{r}) = (3/4\pi\rho_1(\mathbf{r}))^{1/3}$ is the Seitz radius and $\alpha = 0.769$ is a parameter which we have fitted to noble gas data (see section 4). This completes the model for the spherically-averaged exchange-correlation hole for an unpolarized system. We notice again that it is a function of only the *local density*. The exchange-correlation potential energy, Eq. (2.11), obtained from this is again a *local density functional*:

$$\begin{aligned}
\mathrm{U}_{\mathrm{XC}}^{\mathrm{mod}} &= -\left(\frac{1}{2}\right)^{1/3} \int \mathrm{d}\mathbf{r}\rho_1^{4/3}(\mathbf{r}) \left(1+\alpha\left(\frac{3}{4\pi\rho_1(\mathbf{r})}\right)^{1/3}\right)^{1/3} \\
&\approx -\left(\frac{1}{2}\right)^{1/3} \int \mathrm{d}\mathbf{r}\rho_1^{4/3}(\mathbf{r}) - \frac{\alpha}{3}\left(\frac{3}{8\pi}\right)^{1/3} \mathrm{N} \\
&\approx \mathrm{U}_{\mathrm{X}}^{\mathrm{mod}} - 0.126\mathrm{N}\,,
\end{aligned} \tag{2.26}$$

where we expanded around high-density in the second step. Our model thus predicts the potential correlation energy is about 3eV per electron. Again, despite the exchange-correlation energy involving non-local interactions between particles, our model, derived from the basic property of normalization, and with the help of a good local approximation for the ontop hole, results in the exchange-correlation energy depending only on the density. This is much simpler than the exact expression.

These results are essentially the physical reasons behind the success of the X_α method of Slater [15], from around the middle of the last century. Our model is not accurate enough to perform state-of-the-art quantum chemical calculations, but is simply meant to demonstrate the plausibility that a local density functional, based on a picture of the exchange-correlation hole, can give reasonable results for electronic structure calculations.

In Table 3.1 we list results for three noble gas atoms. As in the case of exchange, our rough model gives a fair estimate of $\mathrm{U_{XC}}$, but now is an overestimate rather than an underestimate, and the fractional errors are larger. However, a much more appropriate approximation is *the* local density approximation (LDA) [4], where the exchange and correlation holes are taken from those of a uniform gas. This yields similar formulas and similar results (see Table 3.1)):

$$\mathrm{U_X^{LDA}} = -\frac{3}{4\pi}(3\pi^2)^{1/3}\int d\mathbf{r}\,\mathrm{n}^{4/3}(\mathbf{r}) \approx -0.739\int d\mathbf{r}\,\mathrm{n}^{4/3}(\mathbf{r})\,, \tag{2.27}$$

$$\mathrm{U_C^{LDA}} = \int d\mathbf{r}\;\mathrm{u_C^{unif}}(\mathrm{n}(\mathbf{r}))\,, \tag{2.28}$$

where $\mathrm{u_C^{unif}}(\mathrm{n})$ is the known potential correlation energy density of the uniform electron gas [13]. Note that the fractional errors for $\mathrm{U_{XC}}$ in LDA are less than those for $\mathrm{U_X}$. Correlation makes the hole grow deeper (with the Coulomb interaction, all electrons try to avoid each other), so that Eq. (2.24) implies that the exchange-correlation hole is more localized than the exchange-hole. This is behind the characteristic cancellation of errors between exchange and correlation contributions to the energy. This is not the case for our rough model, whose success is somewhat fortuitous: although the sum-rule property is built in, our model hole is not the hole of a real system so other properties are violated. Moreover the fitting of parameter α is somewhat ad hoc and will be discussed further in the next section. The uniform gas is the *only* system for which a local approximation is exact, and has the added justification that the holes are being taken from another interacting quantum-mechanical system. If there are further important universal rules of which we are currently unaware, these might be built in, since such rules will also be satisfied by the uniform electron gas. For example, the electron-electron cusp condition [16] implies that the first derivative with respect to u of the exchange-correlation hole is simply related to the ontop hole at that point:

$$\left.\frac{\partial}{\partial \mathrm{u}}\right|_{\mathrm{u}=0} \rho_{\mathrm{XC}}^{\mathrm{sph}}(\mathbf{r},\mathrm{u}) = \rho_1(\mathbf{r}) + \rho_{\mathrm{XC}}(\mathbf{r},\mathbf{r})\,. \tag{2.29}$$

This is a universal condition, and so is satisfied by the local density approximation. (Incidentally, Eq. (2.29) is not satisfied by our simple gaussian model which rises from the ontop value as u^2 rather than u). Thus any calculation within LDA is based on a model pair density which exactly satisfies the electron-electron cusp condition. How many wavefunction calculations can you say that about? We describe LDA as a non-empirical approximation, because all inputs come only from properties of an ideal system, the uniform electron gas. On the other hand, remember that the security of the variational principle is relinquished once we make direct models for the pair density.

3. EXACT DENSITY FUNCTIONAL THEORY (DFT)

In the previous section, the pair density was crudely modelled by a local functional of the spin-densities. Now we show how in principle an exact theory can be constructed, in which the equations to be solved are the non-interacting Kohn-Sham equations [4], rather than the far more complex Schrödinger equation (1).

Hohenberg and Kohn in 1964 [3] had the revolutionary realization that *all* properties of a time-independent, interacting system of many identical particles are completely determined by the ground-state density. This was shown by proving that there is a unique correspondence between the ground state density and the external potential for a given interparticle interaction. Everything, including the ground-state energy, excited-state energies, static response properties, is a functional of the ground-state density. (We note that the Hohenberg-Kohn theorem can be generalized to spin-densities, which is necessary when the external potential is spin-dependent. In fact, modern DFT calculations use approximate spin-density functionals, which tend to be more accurate for spin-polarized systems than their total density-functional counterparts (even for spin-independent potentials).)

In particular, all the energy components of Eq. (1) are functionals of the density:

$$\mathrm{E}[\rho_1] = \mathrm{T}[\rho_1] + \mathrm{V}_{\mathrm{ee}}[\rho_1] + \mathrm{V}_{\mathrm{ext}}[\rho_1]\,, \tag{3.1}$$

and the exact ground-state density is found by minimizing this energy with respect to ρ_1, keeping the number of particles fixed:

$$\frac{\delta \mathrm{E}[\rho_1]}{\delta \rho_1(\mathbf{r})} = \mu\,, \tag{3.2}$$

where μ is the chemical potential. If we could find accurate functionals to implement this, a single equation directly for the density ρ_1 could be solved for any electronic structure problem. Unfortunately, no sufficiently accurate density functional approximation for the kinetic energy is known. To get around this, Kohn and Sham showed that each interacting system of N particles can be mapped on to a non-interacting system of N particles, where, by solving a one-electron Schrödinger-like equation and occupying N orbitals, one obtains the same density as that of the interacting system. The Kohn-Sham (KS) equations

$$\left(-\nabla^2/2 + \mathrm{v_S}([\rho_1], \mathbf{r})\right) \phi_\mathrm{i}(\mathbf{r}) = \epsilon_\mathrm{i} \phi_\mathrm{i}(\mathbf{r}) \tag{3.3}$$

must be solved self-consistently since the potential appearing in the equations is a functional of the density. The interacting (and non-interacting) density is $\rho_1(\mathbf{r}) = \sum_{\mathrm{i\ occ.}} |\phi_\mathrm{i}(\mathbf{r})|^2$. In contrast to traditional wavefunction techniques which typically scale rapidly with the number of particles, density functional methods scale as $\approx \mathrm{N}^2 - \mathrm{N}^3$ (or less, see Ref. [9, 17]). The total energy of the interacting system is then rewritten as

$$\mathrm{E}[\rho_1] = \mathrm{T_S}[\rho_1] + \mathrm{U}[\rho_1] + \mathrm{E_{XC}}[\rho_1] + \mathrm{V_{ext}}[\rho_1]\,, \tag{3.4}$$

where $\mathrm{T_S}[\rho_1] = -1/2 \int d\mathbf{r} \sum_{\mathrm{i\ occ.}} \phi_\mathrm{i}^* \nabla^2 \phi_\mathrm{i}$ is the kinetic energy of the non-interacting system. U is the Hartree energy, Eq. (2.8), and $\mathrm{E_{XC}}$ is the exchange-correlation energy whose potential part $\mathrm{U_{XC}}$ we met in the section 2 but now expressed as a functional of the density and whose kinetic part describes the correction to the non-interacting kinetic energy due to interactions. These three functionals are universal in that they are the same for all Coulomb-interacting fermion systems no matter what the external potentials are. Minimizing Eq. (3.4) we find the Kohn-Sham potential is the functional derivative

$$\begin{aligned}
\mathrm{v_S}([\rho_1], \mathbf{r}) &= \frac{\delta(\mathrm{V_{ext}}[\rho_1] + \mathrm{U}[\rho_1] + \mathrm{E_{XC}}[\rho_1])}{\delta\rho_1(\mathbf{r})} \\
&= \mathrm{v_{ext}}(\mathbf{r}) + \mathrm{v_H}([\rho_1], \mathbf{r}) + \mathrm{v_{XC}}([\rho_1], \mathbf{r})\,,
\end{aligned} \tag{3.5}$$

where $\mathrm{v_H}([\rho_1], \mathbf{r})$ is the Hartree potential as before, $\mathrm{v_{ext}}(\mathbf{r})$ is the one-body external potential, and $\mathrm{v_{XC}}([\rho_1], \mathbf{r}) = \delta \mathrm{E_{XC}}/\delta\rho_1(\mathbf{r})$ is the exchange-correlation potential. Eq. (3.5) is *exact* and the first result of modern density functional theory.

Our earliest lessons in quantum mechanics taught us that it is the wavefunction that provides the complete description of the system, nothing more, nothing less. Yet, it appears here that DFT has traded in this function of 3N complex variables for the much simpler one-particle density, a function of just three real variables. The complexity of the problem is contained in the functional $\mathrm{E_{XC}}[\rho_1]$, for which in general, approximations must be made.

What does the Kohn-Sham potential look like? As a simple example, we have plotted the exact $\mathrm{v_S}(\mathbf{r})$ for the Helium atom in figure 3.3. In the ground state, the two electrons occupy the same spatial state with opposite spins. However this is not the ground state of the potential $\mathrm{v_S}(\mathbf{r})$ whose energy ϵ_o is indicated in the figure, nor

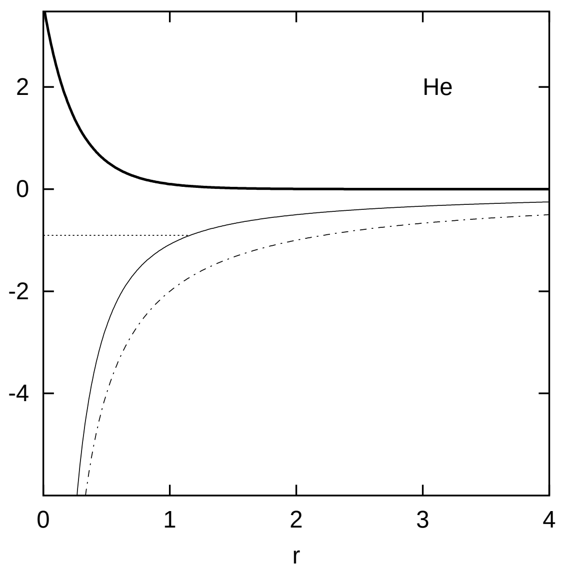

Figure 3.3 The Kohn-Sham potential (thin solid line) for helium and the external potential $-2/\mathrm{r}$ (dash-dotted line). The thick solid line is the ground-state density. The dotted line is the lowest energy eigenvalue of the Kohn-Sham potential.

is its energy equal to $2\epsilon_{\mathrm{o}}$. $\mathrm{v_S}(\mathbf{r})$ is a fictitious potential for the interacting system, whose only defined connection with reality is that its ground-state *density* for non-interacting electrons is equal to that of the true interacting system. The true energy of the physical system is $\mathrm{E} = \sum \epsilon_{\mathrm{i}} - \mathrm{U}[\rho_1] - \int \mathbf{dr}\rho_1(\mathbf{r})\mathrm{v_{XC}}(\mathbf{r}) + \mathrm{E_{XC}}[\rho_1]$.

The nature of the pair density is of particular importance for the calculation of the ground state energy. We saw in section 2 how properties of the pair density were enough to determine an approximate density functional for the exchange-correlation potential energy and potential. For more sophisticated density functional approximations, these properties (and others) are a guide to their construction and effectiveness. So although the density is the main player of DFT, the pair density plays a very important hidden supporting role.

Other exact properties whose satisfaction indicates the accuracy of density functional approximations include behavior under uniform scaling to the high and low density limits [18] and the Lieb-Oxford bound on the exchange-correlation potential energy [19].

The importance of *exact* density functional theory as distinct from the intuitive arguments given in section 2, is that it provides insight into how wavefunction knowledge can be translated into functional approximations, for use in the field. It also tells us the limitations of Kohn-Sham ground-state calculations. For example, the unoccupied orbitals in the He figure are *not* the true excitations of the He atom, even though they are of the KS system. (However, time-dependent DFT *does* tell us how to correct these eigenvalues to turn them into excitation energies [20]).

As mentioned above, the exchange-correlation energy, defined to make Eq. (3.4) exact, contains not only the potential contribution of section 2, but also a kinetic contribution:

$$\mathrm{E_{XC}}[\rho_1] = \mathrm{T}[\rho_1] - \mathrm{T_S}[\rho_1] + \mathrm{V_{ee}}[\rho_1] - \mathrm{U}[\rho_1]\,, \tag{3.6}$$

which arises from the small but significant difference between the kinetic energy in the true system T and in the Kohn-Sham analog $\mathrm{T_S}$. This would appear to require the difference of one-particle density matrices to evaluate, yet our title focuses solely on the pair density. This is because density functional methods have an extremely elegant way to *incorporate* these effects in a pair-density description, through the *adiabatic connection* of DFT [21, 22, 11, 8]. Consider the following Hamiltonian

$$\hat{\mathrm{H}}^\lambda = \hat{\mathrm{T}} + \lambda\hat{\mathrm{V}}_{\mathrm{ee}} + \hat{\mathrm{V}}^\lambda_{\mathrm{ext}}\,, \tag{3.7}$$

where, $\mathrm{V}^\lambda_{\mathrm{ext}}$ is a one-body potential adjusted to give the same ground-state density as the parameter λ is varied. The true interacting system is obtained by taking $\lambda = 1$, whereas the non-interacting exchange limit corresponds to $\lambda = 0$; thus this Hamiltonian provides a smooth pathway between a non-interacting system and the true interacting system, with $\mathrm{V}^\lambda_{\mathrm{ext}}$ chosen to preserve the same density throughout the pathway. This is called the adiabatic connection and λ is called the coupling-constant. Adiabatic connection can also be done of course in a wavefunction picture where one would follow the changing character of the wavefunction as correlation is turned on. For example, there would be a dramatic change in Ψ near $\lambda = 0$ for systems with large static correlation [23]. In DFT, rather than Ψ being the subject, the density ρ_1 is, and, in contrast, this remains the same throughout the connection. It is the functionals which change character.

Defining $\Psi^\lambda[\rho_1]$ as the wavefunction for Hamiltonian H^λ which yields the density $\rho_1(\mathbf{r})$ [22], we have

$$\begin{aligned}\mathrm{E_{XC}}[\rho_1] &\equiv \langle\Psi^{\lambda=1}[\rho_1]|\hat{\mathrm{T}} + \hat{\mathrm{V}}_{\mathrm{ee}}|\Psi^{\lambda=1}[\rho_1]\rangle - \langle\Psi^{\lambda=0}[\rho_1]|\hat{\mathrm{T}}|\Psi^{\lambda=0}[\rho_1]\rangle - \mathrm{U}[\rho_1]\\ &= \int_0^1 \mathrm{d}\lambda\langle\Psi^\lambda[\rho_1]|\mathrm{V}_{\mathrm{ee}}|\Psi^\lambda[\rho_1]\rangle - \mathrm{U}[\rho_1]\,, \end{aligned} \tag{3.8}$$

where, in the last step, we have invoked the Hellman-Feynman theorem [22, 8] and the adiabatic connection has adsorbed the kinetic term in the interaction energy into a potential-like term. Expressing $\mathrm{V_{ee}}$ in terms of the pair density (the last term in Eq. (2.2) but with ρ_2 being the pair density at coupling-constant λ) and therefore in terms of the exchange-correlation hole (Eq. (2.6)), we arrive at

$$\mathrm{E_{XC}}[\rho_1] = \frac{1}{2}\int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{r}' \frac{\rho_1(\mathbf{r})\overline{\rho}_{\mathrm{XC}}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,, \tag{3.9}$$

where the coupling-constant averaged exchange-correlation hole is

$$\overline{\rho}_{\mathrm{XC}}(\mathbf{r},\mathbf{r}') = \int_0^1 \mathrm{d}\lambda \rho_{\mathrm{XC}}^{\lambda}(\mathbf{r},\mathbf{r}')\,. \tag{3.10}$$

Note that $\rho_{\mathrm{XC}}^{\lambda}$ is defined through the definition of the pair density at λ, $\rho_2^{\lambda}(\mathbf{r},\mathbf{r}') = \rho_1(\mathbf{r})(\rho(\mathbf{r}') + \rho_{\mathrm{XC}}^{\lambda}(\mathbf{r},\mathbf{r}'))/2\,.$ The normalization and positivity conditions become

$$\int \mathrm{d}\mathbf{r}'\overline{\rho}_{\mathrm{XC}}(\mathbf{r},\mathbf{r}')) = -1 \tag{3.11}$$

and

$$\overline{\rho}_{\mathrm{XC}}(\mathbf{r},\mathbf{r}')) \geq -\rho_1(\mathbf{r})\,. \tag{3.12}$$

4. OLD FAITHFUL: THE LOCAL DENSITY APPROXIMATION

Recall the crude models of section 2. For the purposes of the exchange-correlation energy calculation, we would model the spherically averaged, coupling-constant averaged exchange-correlation hole, Again, choosing a gaussian form, requiring normalization, and using the high-density limit of the uniform gas to provide the ontop hole, we finally arrive at

$$\mathrm{E_{XC}^{mod}} = \mathrm{U_X^{mod}} - 0.063\mathrm{N}\,. \tag{4.1}$$

So $\mathrm{E_C^{mod}} = \mathrm{T_C^{mod}} + \mathrm{U_c^{mod}} = \mathrm{E_{XC}^{mod}} - \mathrm{U_X^{mod}}$ is about 1.5 eV per electron. Table 3.2 shows the results for the first three noble gas atoms. The parameter α used for the ontop hole in the calculation of Eqs. (2.26) and (4.1) was obtained by minimizing the mean absolute error of our model for $\mathrm{E_{XC}^{mod}}$ for these three atoms. The fractional error is indeed very small but it is not systematic. The point of our model was to demonstrate the plausibility, from a wavefunction perspective, of functionals which depend only on the density but its numerical success is

	E_{XC}	E_{XC}^{mod}	E_{XC}^{LDA}
He	-1.067	-1.076	-0.999
Be	-2.770	-2.748	-2.546
Ne	-12.478	-12.478	-11.763

Table 3.2 Exchange-correlation energies for the first three noble gas atoms, calculated exactly, in our model, and in LDA.

rather fortuitous. The hole we obtained was not the hole of any physical system. Although it satisfied some fundamental properties suggested by the underlying wavefunction, it violates other properties; moreover our need for an empirical fitting of one parameter in E_{XC} and U_{XC} is not entirely satisfactory. It is more important to get reliable results and so we embrace *the* local density approximation much more (see section 2 also).

Also listed in Table 3.2 are the energies from the local density approximation. This, or for spin-polarized systems, the local spin density approximation (LSD), is the simplest density functional. The energy functionals are those for the uniform electron gas, except with the constant electron gas density ρ_{1o} replaced by the local density of the inhomogeneous interacting system $\rho_1(\mathbf{r})$ (or, the constant spin-densities replaced by the local $\rho_{1\uparrow}(\mathbf{r}), \rho_{1\downarrow}(\mathbf{r})$ in the case of LSD). The pair density, or hole, of the inhomogeneous system is approximated by the hole of the uniform electron gas with density that of the local density; because the uniform electron gas is a physical system, its hole satisfies the conditions Eqs. (2.13), (2.15), (2.16), (2.23), (2.24) among others that physical holes satisfy and therefore so does the LSD-approximated hole of the inhomogeneous system. Regions where the density is not slowly-varying, such as near the nucleus or in the tunneling tail, are unweighted by the system average. These reasons, together with the fact that the details of the hole are not important for the purposes of the energy calculation, as long as its system and spherical average are reasonable, is a large part of why this very simple approximation works quite well even for inhomogeneous systems. In figure 3.4 we have plotted the exact Kohn-Sham potential for helium and the LSD potential. Notice that despite their significant difference, the LSD energy and exact energy are very close. This is a reflection of how integrated properties such as energies can be very close even when originating from quite different functions.

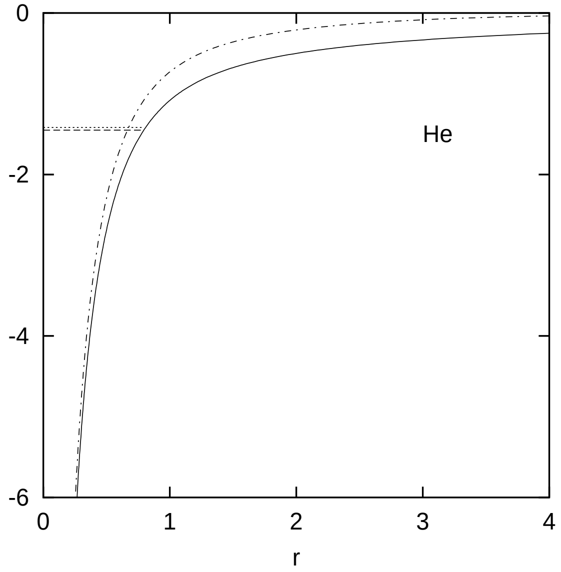

Figure 3.4 The exact Kohn-Sham potential (solid line) for helium and the LSD approximation to it (dash-dotted line). Also shown are half the exact ground state energy (dashed line) and half the LSD energy (dotted line).

Since the exact ontop exchange hole is a function of only the spin densities (Eq. 2.17), the LSD ontop exchange hole is exact (when there is no degeneracy in the Kohn-Sham system). The LSD ontop correlation hole is not generally exact, but it is often a good approximation. It is exact in certain limits: when the density is uniform, in the high-density limit where exchange dominates [24], and in the low-density and fully polarized limits where the electrons avoid each other. As discussed earlier, some cancellation of errors from correlation and exchange result in the local approximation improving through the adiabatic connection.

LSD gives pretty good results for E_{XC} for relatively little effort as discussed above (much like the popular drug of the same name). Especially for larger systems and smoother densities, LSD performs increasingly well and has long been the main-stay of solid-state calculations. Its simple form is often not accurate enough when the system has significant density gradients and in the next section we discuss gradient expansion methods which have been developed to deal with this. Although LSD is faithful to the normalization conditions required by the underlying pair density, it violates other exact conditions. For example, the behavior of the correlation energy under scaling to the high-density limit is incorrect [24] and it does not display the derivative discontinuity [25] at integer changes of particle number. The LSD exchange-correlation potential does not have the correct $-1/\mathrm{r}$ decay at large r for finite systems [26]. LSD also ails under self-interaction error as do typical local functionals. The functionals may work well for many-electron systems but embarrassingly fail to be exact for the simplest case of one electron. Consider the terms making up the energy Eq. (3.4). One electron does not interact with itself so $\mathrm{E_{XC}}$ must exactly cancel the self-interaction present in the Hartree term U:

$$\mathrm{U}[\rho_1] + \mathrm{E_X}[\rho_1] = 0\,, \qquad \mathrm{E_C}[\rho_1] = 0 \qquad (\mathrm{one-electron})\,, \tag{4.2}$$

and similarly for the potentials

$$\mathrm{v_H}([\rho_1];\mathbf{r}) + \mathrm{v_X}([\rho_1];\mathbf{r}) = 0\,, \qquad \mathrm{v_C}([\rho_1];\mathbf{r}) = 0 \qquad (\mathrm{one-electron})\,. \tag{4.3}$$

However, most approximate functionals do not satisfy these conditions. The self-interaction error for many systems is relatively small, but there are some cases where the error is drastic, for example for the hydrogen molecular ion, H_2^+ [27]. Corrections to this are discussed in the next section.

For more discussion on LSD and an excellent review of DFT see Ref. [7].

5. IMPROVING ON THE LOCAL DENSITY APPROXIMATION

In this section, we review the largely successful attempts to improve upon LSD, mostly by improving its accuracy, while attempting to retain its reliability. The non-empirical approached has been championed by Perdew, while a pragmatic well-founded alternative has been championed by Becke. Kohn [1] points out that few functionals have been able to systematically improve on LSD bond lengths.

5.1. Gradient expansions

A natural way to improve LSD for inhomogeneous systems was already suggested in Ref. [4]. LSD is considered as the zeroth-order term in a Taylor series for the functional about the uniform density, and higher-order terms are then included. This (or, sometimes, just the two leading terms) is the gradient expansion approximation (GEA) and has also been interpreted as arising from a small-h expansion [28, 29]. The leading correction is at second order and yields

$$\mathrm{E}_{\mathrm{XC}}^{\mathrm{GEA}}[\rho_{1\uparrow},\rho_{1\downarrow}] = \mathrm{E}_{\mathrm{XC}}^{\mathrm{LSD}}[\rho_{1\uparrow},\rho_{1\downarrow}] + \sum_{\sigma,\sigma'}\int d\mathbf{r}\,\mathrm{C}_{\sigma\sigma'}(\rho_{1\uparrow},\rho_{1\downarrow})\frac{\nabla\rho_{1\sigma}}{\rho_{1\sigma}^{2/3}}\cdot\frac{\nabla\rho_{1\sigma'}}{\rho_{1\sigma'}^{2/3}}\,, \tag{5.1}$$

(where we have suppressed the **r**-dependence in the spin-densities inside the integrand to avoid cluttering). The coefficients $\mathrm{C}_{\sigma\sigma'}(\rho_{1,\uparrow}(\mathbf{r}),\rho_{1,\downarrow)}(\mathbf{r})$ are slowly-varying functions of the densities [30, 31]. One can derive them through perturbing the uniform electron gas with a weak, slowly-varying perturbation, finding the linear response of the density, and expressing the second-order reponse of the energy of interest in terms of the change in the density alone [30].

The GEA improves somewhat the exchange energy estimate. However, except for systems of slowly-varying density (which is not the case for typical atomic and molecular systems), GEA degrades the results for the correlation energy and total exchange-correlation energy over that of LSD. This failure is due [32] to the violation of the sum rules on the exchange and correlation holes (Eqs. (2.13), (2.23)). Unlike the LSD hole, the GEA hole is *not* the hole of any physical system, and so many of the exact conditions that LSD satisfies are violated by GEA. $\rho_{\mathrm{X}}^{\mathrm{GEA}}(\mathbf{r},\mathbf{r}+\mathbf{u})$ and $\rho_{\mathrm{C}}^{\mathrm{GEA}}(\mathbf{r},\mathbf{r}+\mathbf{u})$ tend to be more accurate at small separations u than their LSD counterparts are, but are worse at large u where spurious behavior occurs. The long-range Coulomb interaction does not decay away fast enough for the spurious behavior to be insignificant in an energy calculation.

The failure of the gradient expansion for the exchange-correlation energy motivated exploration into what are now called generalized gradient approximations (GGA), where

$$\mathrm{E}_{\mathrm{XC}}^{\mathrm{GGA}}[\rho_{1\uparrow},\rho_{1\downarrow}] = \int d\mathbf{r}\,\mathrm{f}(\rho_{1\uparrow}(\mathbf{r}),\rho_{1\downarrow}(\mathbf{r}),\nabla\rho_{1\uparrow}(\mathbf{r}),\nabla\rho_{1\downarrow}(\mathbf{r}))\,. \tag{5.2}$$

The first GGA was produced in Ref. [33] in an attempt to correct the GEA correlation energy by fitting an E_{C} of a certain GGA form to known correlation energies. The first non-empirical GGA was that of Langreth and Mehl [34], motivated by the work in Ref. [35], which included a wave-vector analysis of E_{XC}. But because LM was constructed within the random-phase-approximation, it does not reduce to LSD when the gradient vanishes, and violates several other exact conditions. In the same spirit, Perdew showed that the exchange hole oscillates without damping at large separations u, violating the condition Eq. (2.16) and the sum rule Eq. (2.13). This led to the PW86 functional [36] where the exchange hole and exchange energy functional are that of GEA but with sharp real-space cut-offs chosen so that the inequality in Eq. (2.16) and Eq. (2.13) are satisfied. The resulting numerically defined GGA is then fitted to an analytic form. The PW86 correlation energy functional involves the wavevector-space cutoff as in Ref. [34] but goes beyond the RPA. PW86 correctly reduces to the uniform gas limits when gradients vanish, but violates some scaling conditions and the Lieb-Oxford bound. The PW91 GGA [37, 38] extends the real-space cut-off construction for exchange to exchange-correlation by introducing another cut-off radius to satisfy Eq. (2.23). Not only does PW91 satisfy the sum-rules on the holes and reduces to the uniform gas limit appropriately, it also satisfies many (but not all) of the scaling relations and the Lieb-Oxford bound.

In 1996, the PBE GGA was introduced [39], which has a much simpler form than PW91. PBE was constructed by writing down a reasonable functional form for the correlation and exchange energies involving the density and its gradient, where the parameters are determined by considering known exact behavior in certain limits *e.g.* where the gradient vanishes or becomes infinite, uniform scaling to the high-density limit, and satisfaction of the Lieb-Oxford bound. Numerically, PBE gives practically identical results to PW91 for most systems, but with a smoother potential.

Most of the gradient approximations above are non-empirical, being derived according to fundamental principles and knowledge of the uniform gas limit. Alongside of this there has also been a more empirical line of development. Becke-exchange (B88 [40]) is a GGA for the exchange energy constucted with a parameter fitted to the exchange energies of atoms. This worked well, improving LSD results for atomic and molecular systems. B88 is very similar to any of the Perdew exchange functionals, but is a little more accurate for the exchange energies of atoms. Often used with B88 is the the Lee-Yang-Parr correlation energy functional [41]. The LYP correlation functional is a density gradient expansion based on the Colle-Salvetti orbital functional for E_C [42], which arose out of an empirically determined model for the pair density (see below). In Ref. [42], correlation is introduced by approximating the pair density as the non-interacting pair density multiplied by a correlation factor. Through a series of approximations, the Colle-Salvetti formula for the correlation energy was derived, involving the density, non-interacting ontop pair density, and the Laplacian of the pair density evaluated at zero separation, together with four constants which were fitted to the Hartree-Fock orbital for helium. By expressing the non-interacting pair density in terms of the density and first order density matrix (*c.f.* Eq. (2.16)), one can express E_C in terms of the density and non-interacting kinetic energy only; a density gradient expansion of the latter as described above then turns E_C into a density gradient functional. This was the work of Ref. [41], which was later written more usefully without the Laplacian [43]. This works well for small molecules and systems with similar density gradients. For the uniform gas, it does poorly, underestimating E_C by as much as half, partly due to missing parallel-spin correlation [44].

Although originally based on the Colle-Salvetti model for the pair density, that model does not remain faithful to the properties that the pair density (or equivalently exchange and correlation holes) must satisfy [45]. For example, the correlation sum rule Eq. (2.23) is violated. In fact the density itself is not normalized correctly. The reader is referred to [45] for a recent detailed study of the Colle-Salvetti wavefunction and these issues.

For an entertaining and enlightening discussion of the relative merits of the empirical and non-empirical approaches, the reader is referred to a comment on PBE [46] and the response [47].

5.2. Hybrids

The adiabatic connection suggests a way to improve over GGA's. The error at the $\lambda = 0$ end of an approximate adiabatic connection curve tends to be larger than the error at the $\lambda = 1$ end. This is because correlation squeezes the hole, making it deeper and more localized so that LSD and GGA's which use only local information become more accurate. The error at the exchange end is a particular problem for systems with large static correlation (*e.g.* when there are near-degeneracies in the Kohn-Sham system), because the steep downward plunge of the true adiabatic connection curve near $\lambda = 0$ is difficult for GGA's to capture [48]. Since E_{XC} is given by the area under this curve, this effect worsens the accuracy of GGA's, which contain only dynamical correlation. This motivates hybrid functionals: by trading a fraction of approximate density functional exchange with exact exchange (but only a fraction), this error is reduced. The fraction to be mixed was first determined empirically by Becke [49], and later justified non-empirically [23, 50]. Recently, the Perdew group has expanded this concept to approximate the $\lambda \to \infty$ limit of the adiabatic connection curve using density functionals, and to interpolate between it and the small-λ regime, to yield accurate correlation energies [51]. In this way, they derive non-empirically results comparable to the best hybrids.

5.3. Weighted density approximation

The weighted density approximation (WDA) attempts to build non-locality into the exchange-correlation energy in the following way: the energy density, rather than being a function of the local density $\rho_1(\mathbf{r})$, is modified to depend on densities in a neighborhood of $\mathbf{r}$ [52, 53]. First note that in terms of the pair correlation function at λ

$$\mathrm{g}^\lambda(\mathbf{r},\mathbf{r}') = \frac{\rho_2^\lambda(\mathbf{r},\mathbf{r}')}{\rho_1(\mathbf{r})\rho_1(\mathbf{r}')}\,, \tag{5.3}$$

the coupling-constant averaged hole is written as

$$\overline{\rho}_{\mathrm{xc}}(\mathbf{r},\mathbf{r}') = \rho_1(\mathbf{r}) \int_0^1 \mathrm{d}\lambda (2\mathrm{g}^\lambda(\mathbf{r},\mathbf{r}') - 1)\,. \tag{5.4}$$

WDA consists of approximating the true pair correlation function by that of the uniform electron gas at a density $\tilde{\rho}_1(\mathbf{r})$ which is determined by imposing the sum-rule

$$\int \mathrm{d}\mathbf{r}' \int_0^1 \mathrm{d}\lambda \left(2\mathrm{g}^{\mathrm{unif},\lambda}(\tilde{\rho}_1(\mathbf{r}); \mathbf{r}-\mathbf{r}') - 1\right) \rho_1(\mathbf{r}') = -1\,. \tag{5.5}$$

Note that the prefactor in Eq. (5.4) is still the true density $\rho_1(\mathbf{r}')$ at the distant point. WDA improves the exchange energy over LDA, but correlation tends not to be improved. One can generalize the idea to spin-polarized systems (WSDA) [54]. Often, producing accurate results for a particular set of systems requires tailoring the model pair correlation function in a way which makes it less accurate for others. The strong non-locality introduced by the distant density seems contrary to the "near-sightedness" principle of Kohn [9].

5.4. Self-interaction correction and meta-GGA's

In Ref. [55] a method was introduced to correct for the self-interaction error orbital by orbital (SIC). One subtracts the left-hand-side of Eqs. (4.2) evaluated with the approximate density functional on the density associated with each spin orbital individually, for every occupied spin orbital, from the approximate density functional value of $\mathrm{E_X}$ and $\mathrm{E_C}$ respectively on the total density. Unfortunately, the resulting orbital functional is not invariant under unitary transformation among the orbitals. A special set of maximally localized SIC orbitals are often used in calculations. The SIC effective potential correctly decays like $-1/\mathrm{r}$ as $\mathrm{r} \to \infty$ in contrast to the exponential decay of the LSD or GGA potentials. The advantages and disadvantages of SIC are discussed in Ref. [27].

Recently, both Becke [56] and Perdew [57] have proposed meta-GGA's. These functionals use the non-interacting kinetic energy density, a slightly more non-local functional than the density, and its gradient to improve upon GGA's. In particular, it allows various self-interaction errors to be corrected, and also allows the functional to distinguish between single bonds and multiple bonds.

6. NEW TECHNOLOGY

As computations get ever faster and the search for greater accuracy broadens, new methods (beyond ground-state Kohn-Sham equations) are developing.

6.1. The optimized effective potential

Although introduced almost half a century ago [58], the optimized effective potential (OEP) method is now understood to be a way of solving the Kohn-Sham equations with an *orbital*-dependent energy functional. In this sense, it is equivalent to exact DFT, as the exact KS orbitals are implicit density functionals. In the same way that the KS equations enabled the density-dependent non-interacting kinetic energy term in the Euler equation to be evaluated exactly in terms of orbitals, the OEP equations allow the density-dependent exchange term in the KS equations to be evaluated exactly in terms of orbitals.

Modern interest in this subject was greatly enhanced by an extremely accurate approximate solution of the complex OEP equations, introduced by Krieger, Li, and Iafrate [59, 60], A thorough review of this subject is given in Ref. [61]. An obvious application of OEP has been to test the Colle-Salvetti orbital-dependent correlation functional, but with disappointing results for molecules, presumably related to its various violations illustrated in Ref. [45]. Very recently, OEP-type calculations have been implemented both for solids [62] and for molecules [63, 64]. A major open problem in DFT is to construct an accurate and reliable orbital approximation for E_C, which can be used with exact exchange, since present approximations include a cancellation of errors between these two. Already meta-GGA's require OEP if their exchange-correlation potential is to be calculated (typically, they are presently used in a post-GGA evaluation of the energy).

6.2. Time-dependent density functional theory

Exact DFT demonstrates that all observables of a time-independent system are functionals of its ground-state density. But some are more easily approximated than others, such as the the ground-state energy in atoms, molecules, and solids. Excited state energies are also functionals of the density [65], but construction of good approximate functionals for their evaluation has proven difficult. Other properties that are very subtle functionals of the ground-state density are the van der Waals forces between separated neutral species and also the stretched H_2 bond.

A new route to these properties is rapidly emerging in the form of time-dependent density functional theory (TDDFT). This is a separate theory, constructed for electrons in *time*-dependent external potentials, leading to time-dependent Kohn-Sham equations. In the linear response regime, one can see how to handle dipole-dipole fluctuations in van der Waals systems [66], fluctuations on long time scales in stretched H_2, and how to correct the transition energies of ground-state Kohn-Sham potentials into true excitations of the system. In all cases, time-dependent functionals must be approximated, and this area is one of intensive and ongoing research.

7. CONCLUSIONS AND ACKNOWLEDGMENTS

Modern DFT is an alternative approach to interacting quantum systems, with an exact and rigorous foundation. The key aim is to translate physical and chemical insight in traditional quantum mechanics into approximate density functionals, so that advantage can be taken of the computational simplification of solving the Kohn-Sham equations rather than the coupled Schrödinger equation. Progress has been made both with and without the use of empirical parameters. In particular, models of the pair density have motivated many improvements in exchange-correlation energy functionals. We hope that this chapter has given a flavor of the rapid progress in developing good approximate functionals for ground-state DFT.

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