in fig. 3.2. Access to this large amount of systematic and accurate data provides a route to approach the phenomenon of catalysis from the "bottom-up", yielding fundamental understanding and insight into catalytic trends.
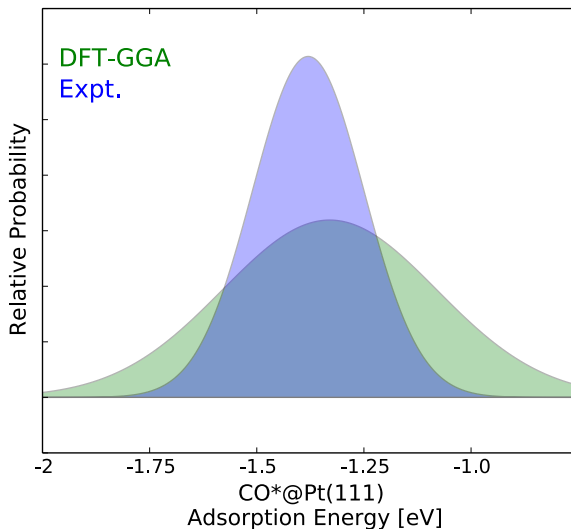

Figure 3.2:   Comparison of DFT and experimentally measured[6] adsorption energy for CO* on a Pt(111) surface. DFT errors are estimated using the BEEF-vdW functional discussed in section 5.1.

3.2   Basics of DFT

3.2.1   Schrödinger's unsolvable equation

The 1933 Nobel Prize in Physics was awarded jointly to Erwin Schrödinger and Paul Dirac for "the discovery of new productive forms of atomic theory." This discovery is encapsulated by the famous Schrödinger equation[4]:

$$i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\Psi \tag{3.1}$$

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[4]The slightly less famous Dirac equation is an extension which accounts for special relativity.

which looks even simpler in its time-independent form:

$$\hat{H}\Psi = E\Psi \tag{3.2}$$

Although the equation looks simple, it is tremendously powerful and complex. This was humbly acknowledged by Dirac, who said that with the development of the relativistic Schrödinger equation "the underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble." [58]

The hidden complexity of the equation is revealed when we examine $\hat{H}$ (the Hamiltonian) and Ψ (the wavefunction) more closely. The Hamiltonian is an operator which depends on the physical system being described[228]. In order to describe the chemistry which governs heterogeneous catalysis (or chemistry in general) we need a Hamiltonian which corresponds to many electrons interacting with multiple nuclei and each other:

$$\hat{H} = \hat{T} \qquad\qquad +\hat{V}_{en} \qquad\qquad +\hat{V}_{ee} \tag{3.3}$$

$$\hat{H} = -\frac{1}{2}\sum_i^{N_e} \nabla_i^2 \qquad +\sum_i^{N_e}\sum_I^{N_n} \frac{-Z_I}{|\vec{r}_i - \vec{R}_I|} \qquad +\frac{1}{2}\sum_i^{N_e}\sum_{j\neq i}^{N_e} \frac{1}{|\vec{r}_i - \vec{r}_j|} \tag{3.4}$$

where ∇^2 is the Laplacian operator, $N_{e/n}$ is the number of electrons/nuclei in the system, Z_I is the charge of nucleus I, and $\vec{r}_i$ ($\vec{R}_I$) is the spatial coordinate of electron i (or nucleus I)[5].[250] The first term ($\hat{T}$) corresponds to the quantum kinetic energy of the interacting electrons, while the latter two terms ($\hat{V}_{en}$ and $\hat{V}_{ee}$) correspond to the potential energy due to Coulombic interactions with the nuclei and other electrons respectively. The expanded Hamiltonian certainly makes the equation seem more

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[5]Note that for brevity "atomic units" are used here. This amounts to the somewhat nonsensical procedure of setting $\hbar = m_e = e = 1/4\pi\epsilon_0 = 1$. In addition, electron spin is neglected in this Hamiltonian. This greatly simplifies the equations by removing constants and makes the physics more apparent, but it is worth remembering that the units and spin need to be rigorously accounted for if the equations are actually going to be solved.

daunting, but there is nothing fundamentally unsolvable about it.

Things become even more complex when the wavefunction, Ψ, is examined. The wavefunction is a complex-valued function which provides a fundamental description of all the electrons in the system. Due to the interacting nature of electrons, the wavefunction depends on the coordinates of all electrons in the system, $\Psi = \Psi(\vec{r}_1, ..., \vec{r}_{N_e}) = \Psi(\vec{r}_i)$. Given that each electron has 3 spatial coordiantes, this means that the wavefunction is a $3N_e$ dimensional function. For example, the electrons of a single Au atom have a 237-dimensional wavefunction.

Furthermore, the critical factor in defining chemistry is the electron-electron interaction. By examining the form of the electron-electron interactions in the Hamiltonian ($\hat{V}_{ee}$) it is clear that this is a multi-body problem which requires simultaneously solving for the positions of all electrons. Even in much simpler classical mechanics it is well-known that there is no analytical solution for problems with more than 3 interacting bodies, which means that our only hope of solving the Schrödinger equation is to use numerical methods (e.g. evaluate the wavefunctions on a grid). If we return to the Au example and assume that we could appropriately sample the wavefunction using a numerical grid with 10 points in each dimension (a bold assumption), we would end up with a grid of 10^{237} points. This is a number so huge that it exceeds the number of atoms in the observable universe[5]! Even the most Panglossian optimist must concede that a computer with this amount of memory is beyond human capacity. Fortunately, all hope is not lost. There are much better ways to approach the problem, leading to approximations to the Schrödinger equation which provide insight into the chemistry and physics of systems far more complex than a single Au atom.

The field of quantum chemistry has developed many sophisticated approaches for representing the wavefunction and approximating the Schrödinger equation (Hartree-Fock, perturbation theory, coupled cluster, etc.). These techniques rely on systematic approximations to the wavefunction and Hamiltonian, so that there is a heirarchy of methods which increase in accuracy as more complexity is added. Such methods are also very computationally intensive, leading to practical limitations in the size of the systems which can be investigated. A deeper analysis is beyond the scope of this

thesis, but more information can be found in numerous textbooks[151, 201].

3.2.2 From wavefunctions to electron density

The wavefunction provides a fundamental description of a system of interacting electrons; however, the wavefunction is not an observable feature of a system. The feature which is (theoretically) observable is the probability that an electron can be found at a particular point in space. For the many-electron system this is closely related to the electron density, which is the expectation value of the number of electrons at some point in space. Mathematically, the electron density can be obtained from the wavefunction[6]:

$$n(\vec{r}) = N \int_{\mathbb{R}^3} \cdots \int_{\mathbb{R}^3} \Psi^*(\vec{r}, \vec{r}_2, ..., \vec{r}_{N_e}) \Psi(\vec{r}, \vec{r}_2, ..., \vec{r}_{N_e}) \, \mathrm{d}\vec{r}_2 \cdots \mathrm{d}\vec{r}_{N_e} \qquad (3.5)$$

$$= N \int_{\mathbb{R}^3} \cdots \int_{\mathbb{R}^3} |\Psi(\vec{r}, \vec{r}_2, ..., \vec{r}_{N_e})|^2 \, \mathrm{d}\vec{r}_2 \cdots \mathrm{d}\vec{r}_{N_e} \qquad (3.6)$$

where Ψ^* is the complex conjugate of Ψ and $|\Psi|^2$ is the probability density of the wavefunction (normalized to 1 by definition). The electron density is a real-valued observable which depends only on 3 spatial dimensions, making it a much easier quantity to work with than the complex-valued 3N-dimensional wavefunction.

The theoretical foundations of DFT lie in two theorems proved by Hohenberg and Kohn [101]. The first Hohenberg-Kohn theorem proves that there is a one-to-one correspondence between the electron density and the ground-state energy[101], and hence the energy is a functional of the electron density[7]. The second Hohenberg-Kohn theorem proves that the electron density that minimizes the energy of this functional is the same electron density obtained from the full solution of the Schrödinger equation. These theorems imply that if the exact energy functional, $E_{exact}[n(\vec{r})]$, is known then the exact electron density can be obtained by minimizing the energy with respect to the electron density $(\frac{\delta E[n_{exact}(\vec{r})]}{\delta n(\vec{r})} = 0)$. This amounts to a 3-dimensional minimization

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[6]The mathematics of this section are amalgamated from two sources where the interested reader may find more details of the derivations[228, 250].

[7]A functional is simply a function of a function which returns a scalar. For example, $F[f(x)] = \int_0^1 f(x) \, \mathrm{d}x$ is a functional of $f(x)$.

problem which is well within the capacity of modern numerical methods (provided the energy functional is not too complex).

Naturally, the new challenge becomes defining the exact energy functional. We know that the energy is the expectation value of the Hamiltonian:

$$E = \int_{\mathbb{R}^3} \cdots \int_{\mathbb{R}^3} \Psi^*(\vec{r}_1, ..., \vec{r}_{N_e}) \hat{H} \Psi(\vec{r}_1, ..., \vec{r}_{N_e}) \, \mathrm{d}\vec{r}_1 \cdots \mathrm{d}\vec{r}_{N_e} \tag{3.7}$$

where $\hat{H}$ is the Hamiltonian from eq. (3.3). We can try to derive the energy functional by writing each term of eq. (3.3) in terms of the electron density. This is relatively easy for interaction between the electrons and nuclei, $\hat{V}_{en}$.

$$E_{ne} = \int_{\mathbb{R}^3} \cdots \int_{\mathbb{R}^3} \Psi^*(\vec{r}_1, ..., \vec{r}_{N_e}) \hat{V}_{en} \Psi(\vec{r}_1, ..., \vec{r}_{N_e}) \, \mathrm{d}\vec{r}_1 \cdots \mathrm{d}\vec{r}_{N_e} \tag{3.8}$$

$$= - \int_{\mathbb{R}^3} n(\vec{r}) \sum_{I}^{N_n} \frac{Z_I}{|\vec{r} - \vec{R}_I|} \, \mathrm{d}\vec{r} \tag{3.9}$$

$$= - \int_{\mathbb{R}^3} n(\vec{r}) V_{ne}(\vec{r}) \, \mathrm{d}\vec{r} \tag{3.10}$$

This term is derived by expansion of the summations, separation of integrals, and indistinguishability of electrons; it remains exact.

The electron-electron interaction portion of the Hamiltonian ($\hat{V}_{ee}$) looks similar at first glance, and can be approached in a similar way:

$$E_{ee} = \int_{\mathbb{R}^3} \cdots \int_{\mathbb{R}^3} \Psi^*(\vec{r}_1, ..., \vec{r}_{N_e}) \hat{V}_{ee} \Psi(\vec{r}_1, ..., \vec{r}_{N_e}) \, \mathrm{d}\vec{r}_1 \cdots \mathrm{d}\vec{r}_{N_e} \tag{3.11}$$

$$= \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{n_2(\vec{q}, \vec{r})}{|\vec{q} - \vec{r}|} \, \mathrm{d}\vec{q} \, \mathrm{d}\vec{r} \tag{3.12}$$

where n_2 is the density correlation function which gives the probability that an electron exists at $\vec{q}$ given that a second electron exists at $\vec{r}$. This two-particle density cannot be written as a function of a single-electron density, and hence some approximation is necessary. If the electrons were uncorrelated then the two-particle density would simply be a product of the two densities. Separating the two-particle density

into this uncorrelated contribution plus some correction yields:

$$n_2(\vec{q}, \vec{r}) = n(\vec{q})n(\vec{r}) + \delta n_2(\vec{q}, \vec{r}) \tag{3.13}$$

which implies:

$$E_{ee} = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{n(\vec{q})n(\vec{r})}{|\vec{q} - \vec{r}|} \, \mathrm{d}\vec{q}\mathrm{d}\vec{r} + \Delta E_{ee} \tag{3.14}$$

This approximation of $n_2(\vec{q}, \vec{r}) = n(\vec{q})n(\vec{r})$ is clearly not correct since we know that electrons obey the Pauli-exclusion principle so that if $\vec{q} = \vec{r}$ then $n_2(\vec{r}, \vec{r}) = 0 \neq n(\vec{r})^2$. This also means that an electron erroneously interacts with itself, as one can clearly see by considering a single-electron system where $n_2(\vec{q}, \vec{r}) = 0 \neq n(\vec{q})n(\vec{r})$, implying that the $i \neq j$ constraint in the second summation of $\hat{V}_{ee}$ is now violated. In principle this issue of electron exchange and self-interaction could be overcome by having the exact ΔE_{ee} which cancels out the contribution.

The final term of eq. (3.3) to evaluate is the kinetic energy, $\hat{T}$. This term is particularly difficult since the Laplacian operator does not commute with the wavefunction or its conjugate, so there is no way to collect a density-like term. In order to overcome this inherently multi-body limitation one of the key assumptions of DFT is used. The assumption is that there exists some collection of N_e non-interacting electrons which have the same ground-state density as the true interacting system.

$$n(\vec{r}) = N \int_{\mathbb{R}^3} \cdots \int_{\mathbb{R}^3} |\Psi(\vec{r}, \vec{r}_2, ..., \vec{r}_{N_e})|^2 \, \mathrm{d}\vec{r}_2 \cdots \mathrm{d}\vec{r}_{N_e} \tag{3.15}$$

$$\overset{\text{assume}}{=} \sum_i^{N_e} |\phi_i(\vec{r})|^2 \tag{3.16}$$

where the $\phi_i(\vec{r})$ are the Kohn-Sham orbitals[122], which are initially unspecified. There is no guarantee that the true density can be expressed in terms of these non-interacting orbitals, but assuming they can then the treatment remains exact.

After introducing the Kohn-Sham orbitals the kinetic energy density can be expressed as:

$$E_T = \int_{\mathbb{R}^3} \cdots \int_{\mathbb{R}^3} \Psi^*(\vec{r}_1, ..., \vec{r}_{N_e}) \hat{T} \Psi(\vec{r}_1, ..., \vec{r}_{N_e}) \, \mathrm{d}\vec{r}_1 \cdots \mathrm{d}\vec{r}_{N_e} \tag{3.17}$$

$$= -\frac{1}{2} \sum_i^{N_e} \int_{\mathbb{R}^3} \phi_i^*(\vec{r}) \nabla^2 \phi_i(\vec{r}) \, \mathrm{d}\vec{r} + \Delta E_T \tag{3.18}$$

where ΔE_T accounts for the fact that the true kinetic energy will differ from the kinetic energy of the non-interacting Kohn-Sham orbitals. Combining everything yields:

$$E = \underbrace{E_T[\phi_i(\vec{r})] + E_{en}[n(\vec{r})] + E_{ee}[n(\vec{r})]}_{\text{"known"}} + \underbrace{\Delta E_{ee}[n_2(\vec{q}, \vec{r})] + \Delta E_T[\Psi(\vec{r}_1, ..., \vec{r}_{N_e})]}_{\text{"unknown"}} \tag{3.19}$$

Technically this expression is still exact, since ΔE_{ee} and ΔE_T are defined to exactly compensate for the approximations we made in E_{ee} and E_T. However, we can see that these unknown exact terms are not functionals of the density. The first Hohenberg-Kohn theorem proves that the energy is a functional of the density, so we know that these energies can also be expressed as a functional of the density[8]. The two unknown correction terms are lumped together and called the "exchange-correlation energy". This name reflects the fact that they compensate for effects of electron exchange in the E_{ee} term (Pauli-repulsion, as discussed earlier) and correlation between electrons (e.g. van-der Waals forces) in the real system which will affect both E_{ee} and E_T.

$$E_{xc}[n(\vec{r})] = \Delta E_{ee}[n_2(\vec{q}, \vec{r})] + \Delta E_T[\Psi(\vec{r}_1, ..., \vec{r}_{N_e})] \tag{3.20}$$

In practice it has proven impossible to find the true $E_{xc}[n(\vec{r})]$, but hundreds of different approximations have been and continue to be developed[122, 190, 191, 92, 275, 274, 34].

The exchange-correlation energy provides the final piece of the energy functional,

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[8]Provided that the true electron density can be expressed in terms of an auxillary system of non-interacing electrons, see eq. (3.16).

which can now be written as:

$$E[\phi_i(\vec{r})] = \underbrace{E_T[\phi_i(\vec{r})] + E_{en}[n(\vec{r})] + E_{ee}[n(\vec{r})]}_{\text{``known''}} + \underbrace{E_{xc}[n(\vec{r})]}_{\text{``unknown''}} \tag{3.21}$$

This is technically a functional of the Kohn-Sham orbitals rather than the density, but it is easy to see that minimizing the function with respect to the Kohn-Sham orbitals is equivalent to minimizing with respect to the density. The functional can be minimized using variational calculus:

$$\frac{\delta E[\phi_i^*(\vec{r})]}{\delta \phi_i^*(\vec{r})} = \frac{\delta E_T[\phi_i^*(\vec{r})]}{\delta \phi_i^*(\vec{r})} + \left[\frac{\delta E_{en}[n(\vec{r})]}{\delta n(\vec{r})} + \frac{\delta E_{ee}[n(\vec{r})]}{\delta n(\vec{r})} + \frac{\delta E_{xc}[n(\vec{r})]}{\delta n(\vec{r})} \right] \frac{\delta n(\vec{r})}{\delta \phi_i^*(\vec{r})} = \epsilon_i \phi_i(\vec{r})$$

$$\tag{3.22}$$

$$-\frac{1}{2}\nabla^2 \phi_i(\vec{r}) + \underbrace{\left[V_{ne}(\vec{r}) + \underbrace{\int_{\mathbb{R}^3} \frac{n(\vec{q})}{|\vec{r}-\vec{q}|} \, d\vec{q}}_{V_{ee}} + \underbrace{\frac{\delta E_{xc}[n(\vec{r})]}{\delta n(\vec{r})}}_{V_{xc}} \right]}_{V_{eff}} \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}) \tag{3.23}$$

$$\left[-\frac{1}{2}\nabla^2 \phi_i(\vec{r}) + V_{eff}(n(\vec{r})) \right] \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}) \tag{3.24}$$

This is the "Kohn-Sham equation" which is the mathematical foundation of DFT. It looks very similar to the Schrödinger equation, with the important distinction that the 3N-dimensional wavefunction, $\Psi(\vec{r}_1, ..., \vec{r}_{N_e})$, is now a set of N 3-dimensional non-interacting Kohn-Sham orbitals, $\phi_i(\vec{r})$. This means that if we re-visit the example of the single Au atom sampled on a grid of 10 points in each dimension we need only 10^3 points, rather than the absurd 10^{237}. In reality a considerably denser samplings (an a number of other techniques) are necessary, but the fundamental reduction in complexity remains.

3.2.3 Applying the Kohn-Sham equations

The Kohn-Sham equations are considerably simpler than the Schrödinger equation, but they are still non-trivial to solve. There are many different computer codes

which are specialized for this task (Quantum ESPRESSO, GPAW, VASP, Dacapo, etc.[82, 63, 16, 125]), each with various implementation techniques which may be advangageous for different situations. The calculations in this thesis were carried out with Quantum ESPRESSO and GPAW, and all details are provided in appendix A. This section instead provides a high-level prescription for how the equations are solved and used to optimize molecular structures.

By examining the V_{eff} term of eq. (3.24) we see that the effective potential depends on the electron density, $n(\vec{r})$. However, eq. (3.16) shows that the density depends on the Kohn-Sham orbitals, $\phi_i(\vec{r})$, which are the solutions to the Kohn-Sham equation. Thus the left-hand side depends on the right-hand side depends on the left-hand side... continuing *ad infinitum*. This circular reference problem is avoided by solving the equations self consistently:

1. Choose an initial trial density, $n(\vec{r})$.

2. Solve eq. (3.24) for $\phi_i(\vec{r})$ using the trial density in V_{eff}.

3. Calculate the electron density of these solutions as $\tilde{n}(\vec{r}) = \sum_i^{N_e} |\phi_i(\vec{r})|^2$.

4. Compare the trial density $n(\vec{r})$ with the solution density $\tilde{n}(\vec{r})$. If they are equal, this density is the ground-state electron density. If they are not equal, mix the two in some way to obtain a new trial density and return to step 2.

This cycle is known as the "self-consistent field" (SCF) or "electronic convergence" cycle and determines the electronic ground state given a set of initial atomic coordinates.

One key assumption thus far has been that we know the exact coordinates of the atomic nuclei. In practice this is rarely the case. This is overcome by exploiting the fact that the forces on nuclei can be obtained from the electron density via the Hellman-Feynmann theorem[71]. The theorem and its proof are omitted here for brevity, but the conclusion is that $\vec{F}_I = \vec{F}_I[n(\vec{r})]$, where $\vec{F}_I$ is the force on nucleus I. Thus, given some initial guess of the atomic coordinates $\vec{R}_I$ the local energy minimum can be obtained by:

1. Choose an initial guess for the atomic coordinates $\vec{R}_I$.

2. Calculate the ground-state energy for the coordinates $\vec{R}_I$ using the SCF cycle outlined above.

3. Calculate the forces on the atomic nuclei $\vec{F}_I[n(\vec{r})]$.

4. Check the size of the forces. If the maximum force is sufficiently small then the geometry is a local minimum. If not, move the atomic nuclei to new positions $\vec{R}'_I$ by assuming the atoms follow Newton's laws of motion and a small amount of time Δt has passed. Set $\vec{R}_I = \vec{R}'_I$ and return to step 2.

In practice more sophisticated algorithms for updating the positions in step 4 are often used, but the Newtonian approach is the most intuitive. When this "geometry optimization" or "ionic convergence" cycle concludes the nuclear coordinates are a local minimum in the ground-state potential energy surface. Note that this local minimum will depend on the initial guess, and is hence not necessarily a global minimum. The structure will also be constrained to the composition of the initial guess since atomic species cannot be created or destroyed. This initial input of atomic coordinates and composition is arguably the largest assumption in any quantum mechanical calculation, though it is rarely mentioned as such.

3.2.4   Limitations of DFT and potential solutions

Density functional theory provides a pragmatic approach to solving the Schrödinger equation, but it suffers from some limitations. First, there is the fundamental limitation that the Hohenberg-Kohn theorems only prove that the ground-state energy is a functional of the electron density. Thus, phenomena such as photo-emission and X-ray absorption which depend on excited states are not expected to be described well within DFT and require advanced methods such as time-dependent DFT (TDDFT)[239] or the GW approximation[108, 227]. Another important caveat of DFT is that the Kohn-Sham orbitals are not equivalent to the true wavefunction, since they actually describe some auxillary system of non-interacting pseudo-electrons rather than the real interacting electrons. Thus the Kohn-Sham eigenvalues, ϵ_i in

eq. (3.24), do not correspond to the true eigenvalues of the system. For this reason the electronic structure obtained from DFT does not correspond to the real electronic structure, although experience has shown that in practice the results from the Kohn-Sham eigenvalues are quite reasonable.

In addition, there is the practical limitation that the true exchange-correlation functional ($E_{xc}[n(\vec{r})]$) is not known. In principle it should be possible to find the exact functional, but despite decades of intensive research the true functional remains elusive [228, 34]. The solution has been to develop many different approximations to $E_{xc}[n(\vec{r})]$. These functionals can provide very accurate results, but the accuracy is typically limited to certain classes of systems. For example, the B3LYP functional is excellent for molecular systems, but performs poorly for solids, while the PBESOL functional exhibits the opposite behavior[19, 192, 275]. This situation is particularly problematic in heterogeneous catalysis, since surface properties involve an interaction between systems of two different classes of atomic systems (molecules and solid surfaces). The solution has been to develop functionals tailored to perfrom well for surface properties. The revised PBE (RPBE) functional of Nørskov and Hammer [92] is one of the earliest and most successful of the surface-tailored functionals, while the recently developed BEEF-vdW functional performs comparably well for surface properties and slightly better for other properties [275]. Both of these functionals are applied in this thesis, and details are provided in appendix A as necessary.

Meanwhile, the quest for the true exchange-correlation functional continues. The most widely used approximations rely on local properties of the electron density, such as its value (LDA), value and first-derivative (GGA), or value, first-, and second-derivatives (meta-GGA). Within these approximations the functional forms of $E_{xc}[n(\vec{r})]$may be derived from some physical limitations[190, 191], fitted to large sets of data[275], or some combination of the two[92]. While the derived functionals tend to be more transferrable, the fitted functionals are typically more accurate. Fitted functionals also provide insight into the limit of how well a given model space will ever perform. The fact that even a meta-GGA functional yields reasonably large errors when fitted to varied data sets[274] indicates that the approach of adding successively more local information is unlikely to lead to the true exchange-correlation functional.

Another approach has been to include non-local information, such as a dual integration over the electron density, in order to improve $E_{xc}[n(\vec{r})]$. This strategy is typically used in order to provide an accurate description of long-range dispersion forces (i.e. van der Waals forces). However, these functionals typically do not perform well for systems where covalent interactions dominate[275, 136]. Combinations of local and non-local information have also been included in $E_{xc}[n(\vec{r})]$ with good results[275], but the results fall considerably short of what would be expected for the exact functional. This suggests that the form of the true $E_{xc}[n(\vec{r})]$ may be exceedingly complicated (perhaps a 3N-dimensional integral?), and at some point the computational cost of evaluating such a complex functional may exceed the cost of methods "beyond" DFT, rendering the true functional practically useless.

An orthogonal strategy is to abandon the constraint that $E_{xc}[n(\vec{r})]$ is a functional of the density and instead compute some approximate form of $E_{xc}[\Psi(\vec{r}_1, ..., \vec{r}_{N_e})]$. For example, the exchange contribution can be computed using a wavefunction-based method such as Hartree-Fock and this "exact" exchange can be included in the exchange-correlation energy[19]. Several functionals exploit such an "exact exchange" (EXX) technique and are typically more accurate but at a significantly increased computational cost[19, 97]. A similar approach can be taken for the correlation energy, using diagrammatic methods such as the random-phase approximation (RPA) in order to properly account for certain types of electron-electron correlations[23, 194, 24, 183]. These approaches further improve the accuracy, but also substantially increase the computational cost. Furthermore, even the most advanced approximations still yield substantial errors, so it is worth considering whether the computational cost is worth the accuracy gain for any given system.