RICE UNIVERSITY

Range-separated hybrids combining a range-separated Perdew-Burke-Ernzerhof functional with exact exchange and random phase approximation correlation

by

Robert Irelan

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Master of Science

APPROVED, THESIS COMMITTEE:

Gustavo E. Scuseria, chair
Robert A. Welch Professor of Chemistry and Professor of Physics and Astronomy

Boris I. Yakobson
Professor of Mechanical Engineering and Materials Science and Chemistry

Cecilia Clementi
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ABSTRACT

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Previous methods of combining a short-range density functional approximation with treatment of the long range using exact exchange and random phase approximation correlation have been extended by replacing a range-separated local density approximation in the short range with a range-separated generalized gradient approximation functional that is generally much more accurate for molecular systems. The coefficients for range separation and for the fraction of random phase approximation correlation are optimized based on thermodynamic test set data. The new functional is shown to retain or markedly improve the accuracy of calculations on test set data compared to previous attempts to combine short-range density functional approximations with long-range exact exchange and random phase approximation correlation while retaining its performance in describing long-range van der Waals interactions.
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Chapter 1

Introduction

The description of weak, noncovalent interactions—the electron-electron interactions between spatially distant electron densities or orbitals—is of fundamental importance for computational chemistry, since this category includes such interactions as hydrogen bonding, van der Waals interactions, dispersion forces, and indeed any intermolecular or long-range intramolecular interactions. Systems where weak interactions are important are ubiquitous, including conformational isomers, solutions, surface reactions, nanomaterials, and biological systems. However, they elude easy modeling. Conventional density functionals, depending on local or semilocal quantities, face considerable difficulty in describing the nonlocal interactions between weakly-overlapping densities that are essential to modeling weak interactions. On the other hand, \textit{ab initio}, wave function-based methods can model weak interactions accurately, but suffer from large basis-set dependency due to their need to explicitly treat the electron-electron cusp, resulting in expensively steep computational scaling.

In the last decade, workers in the density functional community have heavily examined the problem of weak interactions and the dispersion needed to model them, as density functional theory (DFT) has grown more sophisticated and limits of hybrid functionals in molecular calculations have asserted themselves against those who would
discover the perfect exchange-correlation functional. The following section details the major trends in DFT-based dispersion methods in recent years before introducing the random phase approximation (RPA)-correlation approximation that will be developed in this work.

1.1 Methods for modeling dispersion

1.1.1 Explicitly nonlocal functionals

The van der Waals (vdW) functionals of the type proposed by Dion et al. [2] aim to include dispersion effects by explicitly including nonlocal terms in the functional itself. The vdW functionals have continued to be developed, notably by Vydrov and Van Voorhis [3, 4], and have recently achieved quite promising results [3]. However, the accuracy of the calculations done with these correlation functionals depend heavily on the quality of their exchange functionals, and revPBE, the currently-used exchange functional, is not a perfect match for any of the current vdW functionals [5].

1.1.2 Range-separated hybrids with correlation corrections

Excepting the explicitly nonlocal functionals, adding exact partial correlation to a functional involves adapting some sort of post-Hartree-Fock wave function method, often with exact exchange as well. Thus, second order Møller-Plesset perturbation theory (MP2) [6–8], configuration interaction (CI) [9, 10], multi-configuration self-consistent field (MCSCF) [11, 12], and coupled-cluster singles and doubles (CCSD)
[8,13,14] have all been used and been found to model weak interactions accurately [6–8,12,14].

The random phase approximation, nevertheless, has several compelling features that have led to its frequent use in dispersion modeling in recent years. Since recent work [15, 16] which led to a formulation with a computational complexity of $O(N^5)$ in the number of atomic orbitals, the random phase approximation has a cost quite competitive with MP2. Unlike MP2, however, the random phase approximation is non-perturbative, recovers significant static correlation, and is compatible with 100% exact exchange [17]. With these properties, the random phase approximation can easily be used as a companion to a hybrid functional.

1.2 The random phase approximation

The random phase approximation (RPA) originates from the plasmon theory of electron correlation in the electron gas as proposed by Bohm and Pines [18, 19]. Langreth and Perdew [20,21] established the connection of RPA to DFT via the adiabatic-connection formalism.

In the late 1990s and early 2000s, a revival of interest in RPA in the context of density functional theory began, after it had become apparent that local and semilocal density functional approximations were failing to model van der Waals interactions accurately. Andersson [22] and Dobson [23] both exploited the origin of van der Waals interactions in density fluctuations between spatially separated regions, a situation
well described by the nonlocal RPA but not by local and semilocal functionals. Yan et al. [24] presented a GGA correction to RPA, noting the excellent performance of RPA exchange plus correlation and proposing that a combination of RPA and a semilocal correlation functional designed with RPA in mind could potentially reach “chemical accuracy”. It was not, however, until 2001 that Furche [25] presented his method of evaluating RPA based on the Kohn-Sham orbitals (rather than Hartree-Fock).

Since then, the random phase approximation (RPA) has been employed by many as an effective correlation energy correction to semilocal density functional theory in molecules and solids [1, 6, 25–31]. In these schemes, typically exact exchange and RPA correlation are evaluated as a one-shot calculation from Hartree-Fock or Kohn-Sham orbitals. These schemes have the advantages of being fairly accurate for the uniform electron gas in the high-density limit [32] and treating long-range interactions accurately in molecules and solids [33–36], but encounter difficulties in treating short-range interactions with reasonably-sized basis sets [25]. Since this approach by itself underbinds a variety of systems [25, 29, 30, 37–40], various corrections to this basic scheme can be added to ameliorate these issues. Among them are the RPA+ scheme [24], where short-range correlation from a semilocal functional is added; range-separated RPA [1, 30, 31, 41], whereby the exact exchange and RPA correlation are used only in the long range, with semilocal methods being used in the short range; global hybrid functionals [42, 43]; and the use of hybrid reference states and single excitations [44].
We have favored a range-separated approach combining short-range semilocal density functional theory, long-range exact exchange, and long-range direct RPA correlation evaluated as a one-shot correction with the Kohn-Sham orbitals, where direct RPA refers to the neglect of exchange integrals in the particle-hole ring contractions in the correlation problem. Direct RPA has been used because the direct RPA correlation energy is unambiguously defined [45] and because it admits the use of Cholesky decomposition to solve the equations at a cost $O(N^5)$ for $N$ atomic orbitals, a cost that is competitive with MP2 [15,16]. Furthermore, the addition of second-order screened exchange (SOSEX) [1,46,47] to direct RPA to fix one-electron self-interaction error in the direct RPA correlation energy has been pursued because the reduction of this error has been argued to be significant for improving the description of many molecular properties [48], although SOSEX also worsens the description of some static correlation compared to direct RPA [49].

1.3 LC-ωLDA+dRPA and LC-ωLDA+SOSEX

Janesko et al. applied the insights of Furche [15] and Scuseria et al. [16] to create a new range-separated hybrid functional named LC-ωLDA+dRPA [30]. LC-ωLDA+dRPA combines local spin density approximation (LSDA) exchange-correlation in the short range (SR) with long-range Hartree-Fock (HF) exchange and long-range direct random phase approximation (dRPA) correlation in the form

$$E_{xc} = E_{xc}^{SR-LSDA} + E_x^{LR-HF} + c_{RPA} E_c^{LR-dRPA}$$ (1.1)
with range separation and the fraction of RPA exchange each controlled by one empirical parameter. It excels in a variety of thermochemistry benchmarks and gives an excellent description of a variety of weak interactions \([1, 30, 31]\). To remedy the inherent one-electron self-interaction error in dRPA, one can augment dRPA correlation with SOSEX. Benchmarking the augmentation of LC-\(\omega\)LDA+dRPA with SOSEX, which we call LC-\(\omega\)LDA+SOSEX, has shown increased accuracy in describing free atoms compared to LC-\(\omega\)LDA+dRPA but decreased accuracy in describing molecular properties \([1]\); on the other hand, the fraction of Hartree-Fock exchange required is decreased.

Despite the success observed with this range-separated method, it is known that the local density approximation, by itself, is a very poor approximation for describing molecules in areas where the density varies rapidly. In large systems, the poor behavior of LSDA in these limits would likely tarnish the utility of LC-\(\omega\)LDA+dRPA and LC-\(\omega\)LDA+SOSEX, since the covalent and hydrogen bonds for which LSDA performs poorly are more important than in the noncovalently-bound noble-gas dimers and atoms on which these methods have been benchmarked. In addition, it has been observed that, for optimal results, LC-\(\omega\)LDA+dRPA requires a relatively large range separation parameter \(\omega\), which increases basis set dependence and computational time. Furthermore, it has been argued \([15, 24]\) that RPA and GGA correlation energies complement each other, since semilocal functionals can model short-range correlation well while RPA models long-range correlation well, which especially improves the
accuracy of energies involving a change in electron number, such as ionization energies or work functions.

Taking into account these potential disadvantages of LC-\(\omega\)LDA+dRPA and the benefit of combining short-range correlation with RPA, the construction of a range-separated hybrid functional incorporating short-range GGA exchange-correlation, long-range exact exchange, and RPA correlation is a worthwhile path to explore. In this work, the short-range LSDA functional used in LC-\(\omega\)LDA+dRPA and LC-\(\omega\)LDA+SOSEX is replaced by a short-range Perdew-Burke-Ernzerhof (PBE) functional developed by Goll. et al. [13, 14]. These authors have demonstrated the utility of this functional in describing both noble gas-noble gas and alkali metal-noble gas dimers when combined with coupled cluster with singles, doubles, and perturbative triples (CCSD(T)) in the long range. It has previously been demonstrated that results comparable to coupled cluster calculations can be attained using LC-\(\omega\)LDA+dRPA for several systems [1, 30, 31]. It is therefore plausible that modeling the short-range using this range-separated PBE functional will produce more accurate results than the already very good LC-\(\omega\)LDA+dRPA and LC-\(\omega\)LDA+SOSEX methods.
Chapter 2

Theory

Before the LC-ωPBE+dRPA and LC-ωPBE+SOSEX functionals are introduced, it is helpful to introduce the basic theory underlying them. This chapter summarizes the foundations of density functional theory, including the Kohn-Sham formulation of it; the different levels of Kohn-Sham approximations; the use of range separation of the Coulomb operator for Kohn-Sham-based approximations; and the random phase approximation from which a portion of exact correlation can be recovered.

2.1 Fundamentals of density functional theory

Density functional theory (DFT), which provides a formally exact method of calculating the exact ground-state energy of an electronic system using the electronic density of the system rather than the wave function, is widely used in computational chemistry for calculations on molecular and solid-state systems. Among the reasons are the formal convenience of working with a scalar quantity, the electron density, rather than a wave function, which is a part of a vector space; the ability to recover a significant part of the exchange and correlation energies at only mean-field (i.e., on the order of Hartree-Fock) cost when using the Kohn-Sham formulation; and the relative ease with which non-density functional corrections can be used to produce even more accurate
results, usually at a cost far less than that of comparable wave function methods by themselves. Because of its ubiquity, the literature on density functional theory is vast; an extensive introduction to density functional theory, as well as references to further explore the field, may be found in Parr and Yang [50].

2.1.1 Hohenberg-Kohn theorems

Given the exact ground-state wave function $\Psi_0$, which determines all of the properties of a given system, it is trivial to obtain the electron density $\rho_\mathbf{r}$ using the following quadrature:

$$\rho(r_1) = N \int \cdots |\Psi_0(x_1, x_2, \ldots x_N)|^2 \, ds_1 \, dx_2 \cdots dx_N \quad (2.1)$$

On the other hand, the supposition that one can obtain $\Psi_0$ given $\rho$ is not obviously true, and it is only in the early 1960s that Hohenberg and Kohn proved that one could indeed do so.

The theoretical underpinning of density functional theory is the two Hohenberg-Kohn (HK) theorems, which state that the ground state energy of an electronic system is a unique functional of the ground-state electron density $\rho(\mathbf{r})$. The first theorem states that the external potential $v(\mathbf{r})$ is determined, up to an additive constant, by $\rho(\mathbf{r})$, and the ground-state energy $E$ is therefore a functional of $\rho$:

$$E[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho]$$

$$= \int \rho(\mathbf{r}) v(\mathbf{r}) \, d\mathbf{r} + F_{HK}[\rho], \quad (2.2)$$

$$F_{HK}[\rho] = T[\rho] + V_{ee}[\rho],$$
where $T[\rho]$, $V_{ne}[\rho]$, and $V_{ee}[\rho]$ are functionals of $\rho$ for, respectively, the total kinetic energy, the potential energy due to external potentials (including those generated by nuclei), and the potential energy due to electron-electron repulsion. The second theorem states that, given a trial density $\tilde{\rho}(\tilde{r})$ such that $\tilde{\rho}(\tilde{r}) \geq 0$ and $\int \tilde{\rho}(\tilde{r}) \, d\tilde{r} = N$, the ground-state energy $E_0 \leq E[\tilde{\rho}]$, where $E[\tilde{\rho}]$ is the functional defined by (2.2). The implication of these theorems is that, given an external potential $v(\tilde{r})$ and a density $\rho(\tilde{r})$, if we know the form of the Hohenberg-Kohn functional $F_{HK}[\rho]$, we can compute the energy of the system $E[\rho]$ using the first theorem, and the second theorem gives us the variational principle we need to refine $E$ and $\rho$. (In fact, although DFT is easiest to formulate when $\rho$ is $v$-representable—corresponding to an antisymmetric ground-state wave function of some external potential $v$—DFT may also be validly formulated for any $\rho$ that is $N$-representable—corresponding to an $N$-electron wave function—a condition that is much easier to prove and is satisfied by reasonable densities.) The rub, of course, is that $F_{HK}$ is not explicitly known in general; the challenge, then, becomes, to discover ways to approximate the DFT problem so that an explicit functional in $\rho$ can be obtained.

### 2.1.2 Kohn-Sham DFT

Among the approaches to solving (2.2) that have been devised, by far the most widely used in quantum chemistry is the Kohn-Sham (KS) method because it provides a practical path to accurate calculations at mean-field cost (i.e., comparable to the
cost of Hartree-Fock). The Kohn-Sham method recasts the DFT problem in terms of orbitals $\psi_i(\vec{r}, s)$; for noninteracting electrons, they are related to the density by

$$
\rho(\vec{r}) = \sum_i \sum_s |\psi_i(\vec{r}, s)|^2,
$$

(2.3)

where $i$ runs over the coordinates of the $N$ electrons and $s$ over the spin degrees of freedom. It is straightforward to write the kinetic energy of the noninteracting system:

$$
T_s[\rho] = \sum_i \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle
$$

(2.4)

The Hamiltonian of this noninteracting system is then

$$
H_s = \sum_i \left(\frac{1}{2} \nabla^2 \right) + \sum_i v_{\text{ext}}(\vec{r}),
$$

(2.5)

where $v_{\text{ext}}$ is the external potential; the exact ground-state wave function of the noninteracting system is a Slater determinant in the orbitals.

The insight of KS theory is to note that the HK equations may be set up such that $T_s[\rho]$ is the exact kinetic energy of the noninteracting problem, which is also a large portion of the exact kinetic energy of the interacting problem, allowing a larger portion of the total energy to be calculated in a known manner than might seem obvious from the original Hohenberg-Kohn theorems. The remainder of the kinetic energy, as well as other nonclassical terms, can then be included in a relatively small correction, which must then be approximated.

To achieve this, the functional $F[\rho]$ from the HK equations is rewritten as

$$
F[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho]
$$

(2.6)
Here, $J[\rho]$ is the classical Coulomb energy of the charge distribution $\rho$,

$$J[\rho] = \frac{1}{2} \int d\vec{r}_1 \, d\vec{r}_2 \, \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{r_{12}},$$

(2.7)

where $r_{12} = |\vec{r}_1 - \vec{r}_2|$ is the interelectronic distance, and $E_{xc}[\rho]$ is the exchange-correlation energy,

$$E_{xc}[\rho] \equiv T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho],$$

(2.8)

which contains the (presumably small) difference between $T_s$ and $T$ as well as the nonclassical part of $V_{ee}$. With this choice of $F[\rho]$, the potential $v(\vec{r})$ in (2.2) is then replaced by the KS effective potential

$$v_{eff}(\vec{r}_1) = v(\vec{r}_1) + \int \frac{\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \, d\vec{r}_2 + v_{xc}(\vec{r}_1)$$

(2.9)

with the exchange-correlation potential

$$v_{xc}(\vec{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})}$$

(2.10)

Finally, because $T_s[\rho]$ is the exact kinetic energy of a system of $N$ electrons moving in the KS effective potential $v_{eff}(\vec{r})$, the orbitals, and thus the density, can be obtained by solving one-electron functions

$$\left[ -\frac{1}{2} \nabla^2 + v_{eff}(\vec{r}) \right] \psi_i = \varepsilon_i \psi_i.$$

(2.11)

From this equation, as well as the HK equations, the energy of the Kohn-Sham determinant is given by

$$E \langle T \rangle - J[\rho] + E_{xc}[\rho] - \int d\vec{r} \, v_{xc}(\vec{r}) \rho(\vec{r}),$$

(2.12)
where \( \langle T \rangle \) is the expectation value of the kinetic energy with respect to the solution of the noninteracting Hamiltonian in (2.5).

It will be helpful here to briefly discuss several topics that are not a part of basic KS theory but play a part in the construction of LC-\( \omega \)PBE+dRPA and LC-\( \omega \)PBE+SOSEX. First of all, although it is not a part of pure KS theory (it is not even a functional of the density), the nonlocal, “exact” or “Hartree-Fock-type” exchange energy plays a major role in the construction of modern Kohn-Sham-based methods, as described below. The exact exchange energy can be defined [51] in terms of the KS spin orbitals \( \psi_k \) as

\[
E_{x}^{HF} = -\frac{1}{2} \sum_{i,j}^{\text{occ}} \int d\vec{r}_1 \, d\vec{r}_2 \, \psi_i(\vec{r}_1) \psi_j(\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \psi_{i}(\vec{r}_2) \psi_{j}(\vec{r}_1). \tag{2.13}
\]

Second, the Kohn-Sham equations shown in (2.11) are spin-unpolarized, with \( \rho_\alpha = \rho_\beta \). Kohn-Sham theory can also be formulated in a spin-polarized form, with \( \rho = \rho_\alpha + \rho_\beta \) but \( \rho_\alpha \neq \rho_\beta \), to treat spin-polarized systems. The extension to the spin-polarized case is straightforward; see Chapter 8 of Parr and Yang for the detailed derivation. The important point is that spin-up and spin-down orbitals are solved for in separate pseudo-eigenvalue KS equations, but the spins are connected through the classical Coulomb (which depends on \( \rho = \rho_\alpha + \rho_\beta \)) and exchange-correlation operators.

Finally, the generalized Kohn-Sham (GKS) scheme [52,53] is often used to construct functionals that are based on the KS formalism but go beyond it by including non-DFT components, as explained in the rest of the chapter. The model Hamiltonian (2.5) of
KS theory is extended via the form

\[ H_0 = T + V_{\text{ext}} + \tilde{V}_{\text{ee}}. \] (2.14)

Here \( T \) denotes the kinetic energy operator, and \( V_{\text{ext}} \) the external potential operator. The new term \( \tilde{V}_{\text{ee}} \) is a model electron-electron interaction operator. With \( \tilde{V}_{\text{ee}} = 0 \), \( H_0 \) gives the Kohn-Sham model Hamiltonian, but the exchange correlation energy \( E_{xc} \) is large; with \( \tilde{V}_{\text{ee}} = V_{\text{ee}} \), the full interaction, \( E_{xc} = 0 \), but of course the Hamiltonian is expensive to solve. The goal of a GKS functional is to choose \( \tilde{V}_{\text{ee}} \) to obtain a more accurate or useful functional in which the nonclassical electron-electron interaction is only needed over a small range, in order to keep computational costs down. A related formal concept is the adiabatic connection, which uses a smooth turning-on of the electron-electron interaction \( V_{\text{ee}} \), usually via a parameter \( \alpha \) for which \( \alpha = 0 \) represents no electron-electron interaction and \( \alpha = 1 \) represents the fully-interacting system.

2.2 Jacob’s ladder: the hierarchy of density functional theory approximations

Although the Hohenberg-Kohn and Kohn-Sham theorems guarantee the existence of exact functionals in the electron density \( \rho(\vec{r}) \), one cannot generally find explicit forms of the exact functionals in practice. Furthermore, it has been found in practice that restricting constructed functionals to explicitly depend only on the local spin densities \( \rho_\sigma(\vec{r}) \), where \( \sigma = \alpha, \beta \) to denote the density incorporating electrons of \( \alpha \) and \( \beta \) spins respectively, does not produce satisfactory results in many cases. Therefore,
density functional approximations usually incorporate, in addition, derivatives of the density, such as the gradient $\nabla \rho_{\sigma}(\vec{r})$ and the kinetic energy $\tau_{\sigma}(\vec{r})$. Furthermore, it has proven advantageous to combine density functional approximations incorporating any of the above-mentioned ingredients with a wave function-based method, retaining the ability of density functionals approximations to provide exchange and correlation energies at mean-field cost while gaining the ability to incorporate exact exchange from Hartree-Fock or a cheap wave function-based correlation energy without having to use an expensive explicitly-correlated wave function method such as coupled cluster or configuration interaction.

Unlike with wave function theory-based methods, there are no procedures by which DFT functionals can be systematically improved, and the development of new functionals is fundamentally a matter of cleverness on the part of their creators. Nevertheless, an informal hierarchy of density functionals due to Perdew and Schmidt, called Jacob’s ladder [54], does exist as an classification of density functionals based on the complexity of the ingredients incorporated into the functional. The functionals higher on the ladder are generally more accurate due to the increasing complexity of the ingredients they incorporate, but the lower level of the ladder serves as a base on which to develop functionals higher on the ladder and generally contains less computationally-demanding functionals.
2.2.1 Local density approximation

The most basic density functional approximations are those incorporating only the local spin-polarized densities $\rho_\alpha(\vec{r})$ at the point $\vec{r}$. In Kohn-Sham DFT, the local spin density approximation (LSDA) of Kohn and Sham is the preferred method for this level of theory; it approximates the exchange-correlation energy density as $\varepsilon_{xc}[\rho_\alpha, \rho_\beta]$ at each point $\vec{r}$, where $\varepsilon_{xc}[\rho_\alpha, \rho_\beta]$ is the exchange-correlation energy density of the uniform electron gas with spin densities $\rho_\alpha$ and $\rho_\beta$ throughout all space.

Since $\varepsilon_{xc}[\rho_\alpha, \rho_\beta]$ is exactly known in the exchange part and accurately parametrized in the correlation, the LSDA is exact for uniform densities and is fairly accurate for solids and solid surfaces, where the uniform electron gas is a reasonable first approximation, but performs much less satisfactorily for molecules, since molecules have quickly-varying densities that fall to 0 at $r = \infty$.

2.2.2 Generalized gradient approximation

The next-highest level of theory, the generalized gradient approximation (GGA), incorporates a dependence on the spin density gradients $(\rho)_\alpha(\vec{r})$, allowing the functional to respond to changes in density in the neighborhood of $\vec{r}$; for this reason, the dependence is called semilocal, as opposed to the local dependence of the density on just the point $\vec{r}$ and the nonlocal dependence of the exact exchange on the entire space. Although one can incorporate the leading correction to LSDA to construct the second-order gradient correction approximation, it seriously overcorrects LSDA,
predicting positive correlation energies for atoms when the correlation energy $E_c$ should satisfy $E_c \leq 0$. A more satisfactory approach is to extend LSDA by incorporating gradient corrections subject to suitable exact constraints that should be satisfied by exchange-correlation functionals, such as is done by the Perdew-Burke-Ernzerhof (PBE) functional.

2.2.3 Meta-generalized gradient approximation

The next ingredient that is generally included is the Kohn-Sham kinetic energy densities $\tau_\alpha(\vec{r})$, whose inclusion is the essential characteristic of the meta-generalized gradient approximation (MGGA). The major advantage of including the kinetic energy density is that one can eliminate self-correlation, the unphysical correlation energy observed in lower levels of theory of a one-electron system with alpha density $\rho_\alpha(\vec{r})$ (and $\rho_\beta(\vec{r}) = 0$) [54]. On the other hand, finding the functional derivative of MGGA functionals is more complicated than doing so for LSDA and GGAs, requiring averaging over the orbitals to form an optimized effective potential as opposed to the simple process of finding functional derivatives for the lower levels of theory [54]. Because of this difficulty, it is much harder to perform self-consistent calculations with MGGAs, for which reason they were not considered for this project.

2.2.4 Hyper-GGAs: Beyond Kohn-Sham

The next-highest rung on Jacob’s ladder incorporates the exact (Hartree-Fock type) exchange energy, usually in some combination with the DFT exchange energy computed
by some Kohn-Sham functional, to construct hyper-GGA functionals. Although Kohn-Sham DFT is formally exact, which would imply that density functional approximations need to explicitly depend only on the electron density and its derivatives, it has generally been found easier to improve the accuracy of DFT calculations by introducing methods adapted from the wave function world, such as exact exchange and exact partial correlation. A theoretical justification for including exact exchange, due to Becke [55], comes from the adiabatic connection formula, which connects the noninteracting Kohn-Sham reference system to the real system. At $\alpha = 0$, the lack of electron-electron interaction implies that the exchange-correlation energy is just the “pure exchange energy of the Slater determinant of the Kohn-Sham orbitals, with no dynamical correlation whatsoever” [55]. Since the $\alpha = 1$ limit of the LSDA exchange energy, being designed to model the electron gas, tends to overbind for molecules, where the electron-electron interaction is effectively decreased, Becke argues that a hybrid of the exact and DFT exchange can model a wide range of electron densities better than DFT exchange alone.

In adding exact exchange to a functional, the DFT correlation energy functional needs to be chosen or adjusted in order to complement the exact exchange energy introduced, since exchange and correlation energy, being of opposite signs, tend to cancel each other to an extent.

Hyper-GGA functionals combining exact exchange with DFT exchange and DFT correlation are the most commonly used functionals today for accurate calculations.
To achieve even higher-accuracy results, some sort of exact partial correlation can be used, in addition to exact exchange, via a wave function method that depends on unoccupied as well as occupied orbitals. By definition, the wave function method must be a post-HF method, which makes the scaling of these hyper-GGAs much more expensive, potentially on the order of the correlated methods that were too expensive in the first place; cleverness, however, may be able to bring down the costs of some of these functionals, as Furche made KS-RPA much less expensive [15]. Many functionals of this type have been identified in chapter 1.

2.3 Range separation

Range-separated density functional approximations divide the Coulomb operator $1/r_{12}$ into separate ranges of the interelectronic distance $r_{12}$ in order to combine the advantages, or, from the opposite point of view, to mitigate the disadvantages, of different sorts of approximations (e.g., semilocal DFT and wave function). In the most basic and usual form of range separation, a global separation of the Coulomb operator into short-range (SR) and long-range (LR) parts is used, with the SR part being treated with semilocal approximations and the LR part with wave function approximations. The goal with this separation is to avoid the electron-electron coalescence cusp in the short range that increases the basis set dependence of wave function methods, which need many Gaussian basis functions near the cusp in order to approximate the infinite cusp with any degree of accuracy. The short-range is then free to be described
by semilocal approximations, which tend to approximate the exchange-correlation energy better in the short range due to being based on the uniform electron gas model, while the long range can benefit from increased accuracy in the exchange and correlation energies from exact (Hartree-Fock type) exchange and explicitly correlated approximations, respectively.

As originally proposed [56,57], range-separation typically divides the Coulomb operator into a SR and LR part

\[ \frac{1}{r_{12}} = \underbrace{1 - g(r_{12}) \left\| \right.}_{\text{SR}} \right. + \underbrace{g(r_{12}) \left\| \right.}_{\text{LR}}, \]  

(2.15)

where \( g(r_{12}) \) is a function defined such that \( g(0) = 0 \) and \( g(\infty) = 1 \). It can now be seen that the minimized expectation value of the original Hamiltonian is equivalent to

\[ H^{LR} + E^{SR}[\rho] \]  

(2.16)

with

\[ H^{LR} = \sum_i h(i) + \sum_{i<j} \frac{g(r_{ij})}{r_{ij}} \]  

(2.17)

and

\[ E^{SR}[\rho] = \min_{\psi_\rho} \langle \psi_\rho | \sum_i h(i) + \sum_{i<j} \frac{1}{r_{ij}} | \psi_\rho \rangle - \min_{\psi_\rho} \langle \psi_\rho | H^{LR} | \psi_\rho \rangle, \]  

(2.18)

where \( \psi_\rho \) is the set of all antisymmetric wave functions yielding the given \( \rho \). Since the first term in (2.18) is just the definition of the Kohn-Sham energy, taking the difference results in

\[ E^{SR}[\rho] = U^{SR}_{c}[\rho] + \int \rho^{SR}_{\text{xc}}(\rho) \, d\vec{r}, \]  

(2.19)
where

\[ U^{SR}_e[\rho] = \int d\vec{r}_1 \ d\vec{r}_2 \rho(r_1) \frac{1 - g(r_{12})}{r_{12}} \rho(r_2) \]  

(2.20)

is the SR Coulomb interaction, and the exchange-correlation energy density \( \varepsilon^{SR}_{xc}(\rho) \) is evaluated with the SR Coulomb interaction as well.

For two-part range separation, both Ref. 56 and Ref. 57 use \( g(r_{12}) = \text{erf}(\omega r_{12}) \), where \( \omega \) is a range-separation parameter with units of bohr\(^{-1}\), due to its smooth interpolation between short and long range and because it can be easily integrated with the Gaussian functions widely used in computational chemistry; for these reasons, this form remains widely used [6, 13, 14, 58–62].

Range-separated hybrid functionals are a commonly-used type of range-separated functional, in which the range-separated electron-electron interaction operator is used to limit the range of the exact exchange energy or potential; often range-separated semilocal functionals are incorporated as well. Since \( \omega \) ranges from 0 (the semilocal limit) to \( \infty \) (the wave function limit), a lower \( \omega \) usually corresponds to a shorter calculation time, since more of the long range can be neglected during the calculation. There is thus an incentive to reduce a high value of \( \omega \) if possible without sacrificing too much accuracy. Both short-range (with interaction operator \( \text{erfc}(\omega r_{12})/r_{12} \)) and long-range (with \( \text{erf}(\omega r_{12})/r_{12} \)) interaction operators have been used to compute exact-exchange corrections, the short-range interaction being generally preferred for solid-state and large-molecule calculations and the long-range preferred for weakly-interacting systems [51].
2.4 The random phase approximation

The random phase approximation (RPA) originates from the plasma theory of electron correlation in the electron gas as proposed by Bohm and Pines [18,19]. Via a canonical transformation of the Hamiltonian, they expressed the many-body problem of the electron gas in terms of oscillations of the electron gas as a whole plus a short-range interaction term, in which interactions between different frequencies are ignored; this approximation is the source of the name “random phase”. The correlation energy of the RPA problem is then calculated as a multiple of the difference in the total energy of the system calculated using the RPA and that using the Tamm-Dancoff approximation to RPA, which includes only single excitations of the electron gas (exactly which multiple to use is a matter of contention; see discussion below and in Ref. 16).

Langreth and Perdew [20,21] and Gunnarsson and Lundqvist [63] established the connection of RPA to DFT via the adiabatic connection formalism. Under this formalism, the Hamiltonian becomes

\[ H^\alpha = T + V^\alpha[\rho] + \alpha V_{ee}. \]  

(2.21)

Here \( T \) denotes the kinetic energy operator. The coupling strength parameter \( \alpha \) controls the strength of \( V_{ee} \), the electron-electron interaction operator, ranging from \( \alpha = 0 \), the noninteracting KS system whose ground state is the Kohn-Sham determinant \( |\Psi_0\rangle \), to \( \alpha = 1 \), the fully-interacting, physical system. \( V^\alpha[\rho] \) serves to constrain the density of the ground state \( \rho^\alpha \) at a given \( \alpha \) to always be that of the fully-interacting
\((\alpha = 1)\) ground state density \(\rho\). The interacting \((\alpha = 1)\) ground-state energy can thus be written as the sum of the expectation value of the physical Hamiltonian \(H_{\alpha=1}\) with respect to the noninteracting ground state plus the correlation energy \(E_c[\rho]\):

\[
E_0[\rho] = \langle \Phi_0[\rho] | H_{\alpha=1} | \Phi_0[\rho] \rangle + E_c[\rho]
\] (2.22)

The form of \(E_c[\rho]\) is not explicitly known, but it can be written as the coupling strength integral

\[
E_c[\rho] = \int_0^1 d\alpha \, W_c^\alpha[\rho],
\] (2.23)

where \(W_c^\alpha\) is the potential energy difference between the noninteracting system and the system interacting with \(\alpha\) strength,

\[
W_c^\alpha[\rho] = \langle \Psi_0^\alpha[\rho] | V_{ee} | \Psi_0^\alpha[\rho] \rangle - \langle \Phi_0[\rho] | V_{ee} | \Phi_0[\rho] \rangle,
\] (2.24)

with \(\Psi_0^\alpha\) the ground-state wave function at coupling strength \(\alpha\). The adiabatic connection formulation may be used to obtain an exact expression for the correlation energy in terms of one-particle quantities; the random phase approximation is then used to approximate the frequency-dependent Hartree-exchange-correlation kernel into a simpler non-frequency-dependent function, including only the bare Coulomb interaction, which is easier to calculate.

Alternatively, the solution to the RPA equations can be obtained by solving the following generalized eigenvalue problem self-consistently \([15, 16]\):

\[
\begin{pmatrix}
A & B \\
-B & -A
\end{pmatrix}
\begin{pmatrix}
X \\
Y
\end{pmatrix}
= \begin{pmatrix}
X \\
Y
\end{pmatrix} \omega.
\] (2.25)
The elements of the RPA matrix are here defined as

\[ A_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + \langle ib||aj \rangle \]  
(2.26a)

\[ B_{ia,jb} = \langle ij||ab \rangle \]  
(2.26b)

where \( \varepsilon \) is a generalized Kohn-Sham orbital energy, indices \( i \) and \( j \) indicate occupied spin orbitals, indices \( a \) and \( b \) indicate virtual spin orbitals, and \( \langle ij||ab \rangle \) is an antisymmetrized two-electron integral in Dirac notation. In the above equations, Multiplying the above by \( X^{-1} \) on the right and using the identity

\[ T = YX^{-1} \]  
(2.27)

allows (2.25) to be written as

\[ B + AT + TA + TBT = 0. \]  
(2.28)

The solution for \( T \) can then be back-substituted to obtain \( X \), \( Y \), and \( \omega \).

Scuseria et al. [16] pointed out that the above equation can be expressed in terms of the ring-CCD equation i.e., coupled cluster with doubles (CCD) but keeping only particle-hole ring contractions. Because of this, the implementation of RPA in computational codes, both the general principles and perhaps the existing code itself, can be adapted relatively easily to solve the RPA equations. In addition, the RPA correlation energy can realistically be obtained from a calculation that scales as \( O(N^5) \) in the number of orbitals [15,16].

The best expression for the correlation energy \( E^{RPA}_c \) of the method just discussed, which we call full RPA (fRPA), has been a matter of uncertainty [64]. The plasmonic
formula suggests the expression

\[ E_{c}^{RPA} = \frac{1}{2} \text{Tr} BT, \]  

(2.29)

while the connection to coupled cluster theory suggests a prefactor of 1/4 rather than 1/2; other methods of calculating \( E_{c}^{RPA} \) also exist [65–67]. To avoid this ambiguity, we use a form of RPA called direct RPA, which neglects the exchange integrals in (2.26). In other words, direct RPA (dRPA) is defined like fRPA, but with the matrix elements defined as

\[ A_{ia,jb} = (\epsilon_{a} - \epsilon_{i})\delta_{ij}\delta_{ab} + \langle ib|aj \rangle \]  

(2.30a)

\[ B_{ia,jb} = \langle ij|ab \rangle \]  

(2.30b)

and the correlation energy \( E_{c}^{dRPA} \) calculated by

\[ E_{c}^{dRPA} = \frac{1}{2} \text{Tr} BT, \]  

(2.31)

with an unambiguous [16] prefactor of 1/2. The dRPA ansatz is useful because the correlation energy is real as long as the orbitals obey the aufbau principle, as opposed to fRPA, where the correlation energy may in general be complex.

Despite its advantages, dRPA’s neglect of exchange causes it to suffer from one-electron self-interaction error. This error can be eliminated by the second-order screened exchange (SOSEX) [1,46,47] correction to direct RPA eliminates this self-interaction error. The dRPA+SOSEX method (abbreviated throughout to “SOSEX” in method names for brevity) solves the dRPA equations for \( T \) as above and then uses
antisymmetrized integrals to calculate the correlation energy:

\[ K_{ia,jb} = \langle ij||ab \rangle \]  \hspace{1cm} (2.32a)

\[ E_{c}^{\text{SOSEX}} = \frac{1}{2} \text{Tr} K T. \]  \hspace{1cm} (2.32b)
Chapter 3

Implementation of LC-\(\omega\)PBE+dRPA

This chapter details the implementation of LC-\(\omega\)PBE+dRPA and LC-\(\omega\)PBE+SOSEX, including the form of the underlying short-range PBE functional and the introduction of RPA correlation.

3.1 Form of the short-range functional

For ease of reference, we define the following quantities for the following section:

- the total density \(\rho = \rho_\alpha + \rho_\beta\)
- the Fermi momentum \(k_F = (3\pi^2\rho)^{1/3}\)
- the dimensionless density gradient \(s = |\nabla\rho|/2k_F\rho\)
- the local Seitz radius \(r_s = \left(\frac{3}{4\pi\rho}\right)^{1/3}\)
- the relative spin polarization \(\zeta = (\rho_\alpha - \rho_\beta)/\rho\)
- the dimensionless density gradient \(t = |\nabla\rho|/2\phi k_s\rho\)
- the spin-scaling factor \(\phi(\zeta) = \frac{1}{2} \left[ (1 + \zeta)^{2/3} + (1 - \zeta)^{2/3} \right]\)
- the Bohr radius \(a_0 = \hbar^2/me^2\)
• the Thomas-Fermi screening wave number \( k_s = \sqrt{4k_F/\rho a_0} \)

The original, full-range PBE functional [68] has the following form:

**Exchange** In PBE, the exchange energy density is obtained by scaling the LSDA exchange energy density \( \varepsilon_x^{LDA}(\rho) \) with an enhancement factor \( F_x^{PBE}(s) \):

\[
E_x^{PBE}[\rho_{\alpha}, \rho_{\beta}] = \int d^3 r \rho \varepsilon_x^{LDA}(\rho_{\alpha}, \rho_{\beta}) F_x^{PBE}(s) \tag{3.1}
\]

Here, \( \sigma = \alpha \) or \( \beta \) depending on the spin being treated, and the total exchange energy of a spin-polarized system is obtained via the spin-scaling relation

\[
E_x^{PBE}[\rho_{\alpha}, \rho_{\beta}] = \frac{1}{2} \left( E_x^{PBE}[2\rho_{\alpha}, 2\nabla \rho_{\alpha}] + E_x^{PBE}[2\rho_{\beta}, 2\nabla \rho_{\beta}] \right). \tag{3.2}
\]

The form of the enhancement factor for PBE is

\[
F_x^{PBE}(s) = 1 + \frac{b^{PBE} s^2}{1 + b^{PBE} s^2/\kappa}, \tag{3.3}
\]

where \( \kappa = 0.804 \) is chosen to satisfy the Lieb-Oxford bound [69], which requires that \( F_x(s) \leq 1.804 \), and \( b^{PBE} \approx 0.21951 \) is chosen to recover the LSDA linear response in regions of slowly-varying density, where LSDA is an excellent approximation.

**Correlation** The PBE correlation energy \( E_c^{PBE}[\rho_{\alpha}, \rho_{\beta}] \), is obtained by applying a gradient correction to the LSDA correlation energy density \( \varepsilon_c^{LDA}(r_s, \zeta) \),

\[
E_c^{PBE}[\rho_{\alpha}, \rho_{\beta}] = \int d^3 r \rho \left[ \varepsilon_c^{LDA}(r_s, \zeta) + H(r_s, \zeta, t) \right], \tag{3.4}
\]
Here \( \rho = \rho_\alpha + \rho_\beta \), In PBE, the form of \( H(r_s, \zeta, t) \) is chosen to be

\[
H^{PBE}(r_s, \zeta, t) = \gamma \phi^3(\zeta) \ln \left[ 1 + \frac{\beta^{PBE}}{t^2} \left( \frac{1 + At^2}{1 + At^2 + A^2 t^4} \right) \right],
\]

(3.5)

where \( \gamma = 0.031091, \beta^{PBE} = 0.066725, \) and

\[
A = \frac{\beta^{PBE}}{\gamma \left[ \exp \left( -\varepsilon^{LDA}(r_s, \zeta) / \left( \gamma \phi^3 \right) \right) - 1 \right]}.
\]

(3.6)

The form of (3.5) is an ansatz constructed to satisfy the following conditions: (1) In the slowly-varying limit (\( t \to 0 \)), \( H \) must reduce to its second-order gradient expansion \( H \to (e^2/a_0)\beta^{PBE} \phi^3 t^2 \); (2) In the rapidly-varying limit (\( t \to \infty \)), the correlation energy must vanish, implying \( H \to -\varepsilon^{LDA}_c \); (3) Under uniform scaling to the high-density limit, \( H \) must cancel out the logarithmic singularity in \( \varepsilon^{LDA}_c \), giving \( H \to (e^2/a_0)\gamma \phi^3 \ln t^2 \).

Goll et al. [13, 14] develop a short-range PBE exchange-correlation functional by fitting their functional to the same constraints as the original PBE functional but using \( \text{erfc}(\omega r_{12})/r_{12} \) as the electron-electron interaction operator; in effect, they replace several constant parameters of the PBE functional (those that they determine to significantly vary with \( \omega \)) with range-dependent functions of \( \omega \) (and possibly of the other explicit arguments \( r_s \) and \( \zeta \)), whose forms are determined by applying analytic expansions of the short-range LSDA exchange-correlation energy to second order to the PBE constraints. For the exchange part, they [13] replace the constant \( b^{PBE} \) with a function dependent on the range-separation parameter \( \omega \),

\[
b(\omega) = \frac{b^{PBE}}{b^T(0)} b^T(\tilde{\omega}) \exp (-\alpha_s) \tilde{\omega}^2,
\]

(3.7)
where $\alpha_x = 19.0$, $\tilde{\omega} = \omega/(2k_F)$ and

$$b^T(\tilde{\omega}) = \frac{-c_1 + c_2 \exp(1/(4\tilde{\omega}^2))}{c_3 + 54c_4 \exp(1/(4\tilde{\omega}^2))},$$

$$c_1 = 1 + 22\tilde{\omega}^2 + 144\tilde{\omega}^4,$$

$$c_2 = 2\tilde{\omega}^2(-7 + 72\tilde{\omega}^2),$$

$$c_3 = -864\tilde{\omega}^4(-1 + 2\tilde{\omega}),$$

$$c_4 = \tilde{\omega}^2\left\{-3 - 24\tilde{\omega}^2 + 32\tilde{\omega}^4 + 8\tilde{\omega}\sqrt{\pi} \text{erf}\left[1/(2\tilde{\omega})\right]\right\}.$$  

(3.8)

The exponential term in (3.7) serves to dampen $b(\omega)$ as $\omega \rightarrow \infty$, $b^T(\tilde{\omega})$ is the expansion of the exchange hole to second order in terms of the density gradient, as determined by Toulouse et al. [70], and the $\frac{b_{\text{PBE}}}{b^T(0)}$ factor ensures that $b(0) = b_{\text{PBE}}$ for the full-range limit $\omega = 0$.

To obtain a short-range correlation energy formula, Goll et al. [14] extend the PBE correlation energy density formula by replacing the LSDA correlation energy density $\varepsilon_c^{LDA}(r_s, \zeta)$ with a range-dependent form $\varepsilon_c^{LDA}(r_s, \zeta, \omega)$ derived by Paziani et al. [62] in both (3.4) and (3.6). In addition, $\beta^{\text{PBE}}$ is parametrized in terms of $\omega$ as

$$\beta(\omega) = \beta^{\text{PBE}} \left(\frac{\varepsilon_c^{LDA}(r_s, \zeta, \omega)}{\varepsilon_c^{LDA}(r_s, \zeta, 0)}\right)^{\alpha_c}$$  

(3.9)

with $\alpha_c = 2.78$; the form of the parametrization is chosen to fit ab initio results for the SR correlation energy of the He atom.
3.2 Construction of the hybrids

Like its predecessors LC-ωLDA+dRPA and LC-ωLDA+SOSEX, the functionals proposed in this work are range-separated global hybrids with a long-range correlation correction.

Recall that, after having evaluated the LR exact exchange and direct RPA correlation from the generalized Kohn-Sham (GKS) reference of the LC-ωLDA calculations, the LC-ωLDA+dRPA exchange-correlation energy is calculated by

$$E_{xc} = E_{xc}^{SR-LSDA} + E_x^{LR-HF} + c_{RPA}E_c^{LR-dRPA}$$

(3.10)

and the LC-ωLDA+SOSEX exchange-correlation energy by

$$E_{xc} = E_{xc}^{SR-LSDA} + E_x^{LR-HF} + c_{SOSEX}E_c^{LR-SOSEX}$$

(3.11)

The short-range LSDA exchange-correlation energy $E_{xc}^{SR-LSDA}$ is calculated by integrating the exchange-correlation energy density $\varepsilon_{xc}^{RS-LSDA}$,

$$E_{xc}^{SR-LSDA} = \int d\mathbf{r} \rho \varepsilon_{xc}^{RS-LSDA}(\mathbf{r})$$

(3.12)

The coefficients $c_{RPA}$ and $c_{SOSEX}$, following Refs. 1, 30, 31, are treated as empirical parameters to account for basis-set incompleteness and other effects not treated by this approximation.

In LC-ωPBE+dRPA and LC-ωPBE+SOSEX, the SR exchange-correlation energy is calculated using Goll’s SR PBE functional instead of the short-range LSDA functional used in the LC-ωLDA-based functionals, but the calculation of the wave function-based
quantities proceeds the same, calculating the long-range exact exchange and direct RPA correlation from the GKS reference state given by Goll’s functional. The total exchange-correlation energy of LC-ωPBE+dRPA is given by

\[ E_{xc} = E_{xc}^{SR-PBE} + E_x^{LR-HF} + c_{RPA} E_{c}^{LR-dRPA}, \] (3.13)

and that of LC-ωPBE+SOSEX by

\[ E_{xc} = E_{xc}^{SR-PBE} + E_x^{LR-HF} + c_{SOSEX} E_{c}^{LR-SOSEX}. \] (3.14)

The coefficients \( c_{RPA} \) and \( c_{SOSEX} \) are still treated as empirical parameters to be varied—note that they are independent of those used for the LC-ωLDA functionals.

### 3.3 Computational details

The LC-ωPBE+dRPA and LC-ωPBE+SOSEX schemes, as defined above, have been implemented in the development version of the GAUSSIAN suite of programs [71]. First, Gaussian solves the GKS equations using the SR PBE functional described in section 3.1, implemented with first derivatives in order to obtain a self-consistent solution. From here, the procedure follows that detailed in Ref. 30 and, regarding the SOSEX-specific details, Ref. 1 for SOSEX. The LR Hartree-Fock exchange is evaluated from the GKS reference obtained using the SR PBE functional, and either LR dRPA (for LC-ωPBE+dRPA) or LR dRPA+SOSEX (for LC-ωPBE+SOSEX) are then calculated from the same GKS reference used to calculate the LR Hartree-Fock exchange; the energies are calculated by (3.13) and (3.14) respectively. Like other
workers [6, 7, 13, 14, 56, 57, 60, 61, 70, 72, 73], we select the range separation parameter \( \omega \) empirically. In addition, following Refs. 1, 30, 31, where it was shown that scaling \( E_{cRPA}^d \) by 1.5 in LC-\( \omega \)LDA+dRPA, reduced the error in many calculations, we explore treating the scaling factor \( c_{RPA} \) as an empirical parameter, and similarly we treat the fraction of long-range SOSEX correlation \( c_{SOSEX} \) as an adjustable parameter.

In general, open shell systems are treated spin unrestricted; the dRPA and SOSEX equations are solved iteratively using direct inversion in the iterative subspace [74] (DIIS) for coupled cluster; and correlated calculations use frozen core electrons. All calculations use the correlation consistent basis sets of Dunning et al. [75].
Chapter 4

Results

In this chapter we optimize the empirical parameters of the LC-\(\omega\)PBE+dRPA and LC-\(\omega\)PBE+SOSEX functionals, and use these optimized parameters to assess the accuracy of the functional for a selection of molecules. This section was originally published as part of a previous paper [76].

4.1 Optimizing \(\omega\) and \(c_{RPA}/c_{SOSEX}\)

The parameters \(\omega\) and \(c_{RPA}/c_{SOSEX}\) were optimized against the mean absolute error (MAE)—the average of the absolute value of the errors between theory and experiment for a set—of several thermochemistry test sets, with calculations done as described above using the cc-pVQZ basis. The initial optimization of \(\omega\) was performed by calculations on the AE6BH6 [77] test set, consisting of six atomization energies (AE6) and six hydrogen transfer barrier heights (BH6), because it requires relatively little computational time while still accurately predicting errors for larger test sets. The test set was computed for \(\omega\) from 0.10 to 1.50 bohr\(^{-1}\) in steps of 0.05, after which the correlation rescaling parameter, \(c_{RPA}\) for LC-\(\omega\)PBE+dRPA and \(c_{SOSEX}\) for LC-\(\omega\)PBE+SOSEX, was varied between 1.00 and 2.00. While writing Refs. 30 and 1, we observed that the MAE for the AE6 test set is on the order of 4.5 kcal/mol and for
the BH6 test set is on the order of 1.5 kcal/mol, using optimized parameters for the LC-\(\omega\)LDA-based functionals. Using LC-\(\omega\)PBE+dRPA and LC-\(\omega\)PBE+SOSEX, we have found that the approximate 3:1 ratio between the AE6 and BH6 MAEs remains for the LC-\(\omega\)PBE-based functionals. Following that example, the following weighted MAE was used to optimize the parameters \(\omega\) and \(c_{\text{RPA}}/c_{\text{SOSEX}}\) in order to put both test sets on an equal footing:

\[
\text{MAE}_{\text{weighted}} = \frac{\text{MAE}_{\text{AE6}}}{1.5} + \frac{\text{MAE}_{\text{BH6}}}{1.5}
\]

The dependence of the AE6, BH6, and weighted MAEs on \(\omega\) and \(c_{\text{RPA}}/c_{\text{SOSEX}}\) is shown in Figures 4.1, 4.2, and 4.3 respectively. A general trend that emerges is that while LC-\(\omega\)PBE+dRPA is relatively insensitive to \(\omega\) over a wide range, it does well only within a relatively narrow band of \(c_{\text{RPA}}\); on the other hand, LC-\(\omega\)PBE+SOSEX performs well over a wider range of \(c_{\text{SOSEX}}\) but a somewhat smaller range of \(\omega\). The most apparent trend is that LC-\(\omega\)PBE+dRPA obtains lower MAEs for both test sets compared to LC-\(\omega\)PBE+SOSEX, although LC-\(\omega\)PBE+SOSEX performs its best with an \(\omega \approx 0.6\), whereas LC-\(\omega\)PBE+dRPA performs better with \(\omega \approx 1.1\). The optimal values of \(\omega\) from these calculations were found to be \(\omega = 1.15\) for LC-\(\omega\)PBE+dRPA and \(\omega = 0.65\) for LC-\(\omega\)PBE+SOSEX. It is also apparent that slightly more LR correlation is required for an optimal description of the AE6 test set as compared to the BH6 test set: the optimal value for \(c_{\text{RPA}}\) is approximately 1.60 for the atomization energies, compared to 1.4 for the barrier heights. A similar difference is observed for the LC-\(\omega\)PBE+SOSEX calculations, albeit less drastic due to the greater tolerance of
the method towards variation of the amount of long-range correlation in general.

Having optimized \( \omega \) with AE6BH6, the scaling parameter was optimized against the mean absolute errors of several larger test sets: the G2-1 test set [78] for atomization energies and the HTBH38/04 [79] and NHTBH38/04 [80] test sets for hydrogen and non-hydrogen transfer barrier heights. As before, a sum of MAEs weighted to put each test set on an equal footing in the optimization,

\[
\text{MAE}_{\text{weighted}} = \frac{\text{MAE}_{G2-1}}{12} + \frac{\text{MAE}_{HTBH38/04}}{3} + \frac{\text{MAE}_{NHTBH38/04}}{5},
\]

was minimized. The optimal \( \omega \) using these basis sets did not change from the results found using the AE6 and BH6 basis sets, but the optimal \( c_{\text{RPA}} \) and \( c_{\text{SOSEX}} \) did change slightly. The optimized parameters used for the remainder of the calculations in this paper are \( \omega = 1.15, c_{\text{RPA}} = 1.63 \) for LC-\( \omega \)PBE+dRPA and \( \omega = 0.65, c_{\text{SOSEX}} = 1.63 \) for LC-\( \omega \)PBE+SOSEX. (The equality of \( c_{\text{RPA}} \) and \( c_{\text{SOSEX}} \) is coincidental.)
Figure 4.2: Contour plot of weighted mean absolute error (kcal/mol) for the BH6 test set vs. $\omega$ and $c_{\text{RPA}}$, weighted according to (4.1). cc-pVQZ basis.

Figure 4.3: Contour plot of weighted mean absolute error (kcal/mol) for the AE6BH6 test set vs. $\omega$ and $c_{\text{RPA}}$, weighted according to (4.1). cc-pVQZ basis.
4.2 Results and Basis Set Dependence

Table 4.1 compares statistical errors in molecular thermochemistry and reaction barriers for LC-\(\omega\)PBE+dRPA and LC-\(\omega\)PBE+SOSEX to several other methods evaluated in previous work [1]. After optimization, both LC-\(\omega\)PBE+dRPA and LC-\(\omega\)PBE+SOSEX perform better than the LC-\(\omega\)LDA functionals with and without correlation rescaling, although LC-\(\omega\)PBE+dRPA performs better than LC-\(\omega\)PBE+SOSEX on all of the test sets except for NHTBH38/04.

Figures 4.4 and 4.5 show counterpoise-corrected dissociation curves for all van der Waals noble gas dimers between He, Ne, and Ar for LC-\(\omega\)PBE+dRPA and LC-\(\omega\)PBE+SOSEX using the parameters optimized from thermochemical data. Accurate curves are computed using the potentials from Ref. 81. While the thermochemically optimized \(c_{\text{RPA}}\) performs very well in predicting the shape and dissociation energy of the noble gas dimer curves, it can be observed that LC-\(\omega\)PBE+SOSEX with its thermochemically optimized \(c_{\text{SOSEX}}\) value significantly overcorrelates and thus overestimates the dissociation energy of all the noble gas dimers. Using \(c_{\text{SOSEX}} = 1.35\) (not shown) produces a much better agreement with the accurate curves, but produces a mean absolute error of 5.6 kcal/mol for the G2-1 set, although the barrier height test sets do not register such a large increase.

Figure 4.6 shows the basis set dependence of LC-\(\omega\)PBE+dRPA and LC-\(\omega\)PBE+SOSEX for the total energy of the N atom and the dissociation energy of \(N_2\). The basis set dependence of both of the above methods is comparable to LC-\(\omega\)LDA+dRPA and weak
Figure 4.4: Counterpoise-corrected dissociation curves of homonuclear noble gas dimers vs. internuclear separation in Bohr. LC-ωLDA+dRPA calculations use ω = 1.20, \( c_{\text{RPA}} = 1.50 \); LC-ωLDA+SOSEX, \( \omega = 1.20 \), \( c_{\text{SOSEX}} = 1.50 \); LC-ωPBE+dRPA, \( \omega = 1.15 \), \( c_{\text{RPA}} = 1.63 \); LC-ωPBE+SOSEX, \( \omega = 0.65 \), \( c_{\text{SOSEX}} = 1.63 \);
Figure 4.5: Counterpoise-corrected dissociation curves of heteronuclear noble gas dimers vs. internuclear separation in Bohr. LC-ωPBE+dRPA calculations use $\omega = 1.15$, $c_{\text{RPA}} = 1.63$; LC-ωPBE+SOSEX, $\omega = 0.65$, $c_{\text{SOSEX}} = 1.63$;
Figure 4.6: Basis set dependence of LC-ωPBE+dRPA and LC-ωPBE+SOSEX. (Top) Total energy of N atom. (Bottom) Dissociation energy of N\textsubscript{2} at the experimental bond length 1.098 Å. The results are calculated with aug-cc-pV\(\zeta\)Z basis sets and shown as the difference between the aug-cc-pV5\(\zeta\)Z energy and the calculated energy. LC-ωLDA+dRPA calculations use ω = 0.50, \(c_{\text{RPA}} = 1.00\); LC-ωPBE+dRPA, ω = 1.15, \(c_{\text{RPA}} = 1.63\); LC-ωPBE+SOSEX, ω = 0.65, \(c_{\text{SOSEX}} = 1.63\);
Table 4.1: Mean absolute errors (kcal/mol) in AE6 and G2-1 atomization energies, BH6 and HTBH38/04 hydrogen transfer barrier heights, and NHTBH38/04 non-hydrogen transfer barrier heights. Previous LC-$\omega$LDA-based results from Ref. 1. No rescaling of correlation energies unless specified in footnote.

<table>
<thead>
<tr>
<th>Method</th>
<th>$\omega$</th>
<th>AE6</th>
<th>G2-1</th>
<th>BH6</th>
<th>HT</th>
<th>NHT</th>
</tr>
</thead>
<tbody>
<tr>
<td>LC-$\omega$LDA</td>
<td>0.5</td>
<td>5.8</td>
<td>5.5</td>
<td>2.3</td>
<td>2.7</td>
<td>5.0</td>
</tr>
<tr>
<td>LC-$\omega$LDA+dRPA</td>
<td>0.7</td>
<td>3.8</td>
<td>4.8</td>
<td>1.7</td>
<td>2.0</td>
<td>4.0</td>
</tr>
<tr>
<td>LC-$\omega$LDA+dRPA$^*$</td>
<td>1.2</td>
<td>6.4</td>
<td>3.0</td>
<td>1.2</td>
<td>1.3</td>
<td>3.8</td>
</tr>
<tr>
<td>LC-$\omega$PBE+dRPA$^+$</td>
<td>1.15</td>
<td>4.4</td>
<td>2.7</td>
<td>1.0</td>
<td>1.0</td>
<td>2.8</td>
</tr>
<tr>
<td>LC-$\omega$LDA+SOSEX</td>
<td>0.6</td>
<td>8.5</td>
<td>4.3</td>
<td>1.9</td>
<td>1.9</td>
<td>3.8</td>
</tr>
<tr>
<td>LC-$\omega$LDA+SOSEX$^\dagger$</td>
<td>1.0</td>
<td>7.2</td>
<td>5.1</td>
<td>2.6</td>
<td>3.1</td>
<td>5.2</td>
</tr>
<tr>
<td>LC-$\omega$PBE+SOSEX$^\ddagger$</td>
<td>0.65</td>
<td>6.0</td>
<td>3.3</td>
<td>1.9</td>
<td>1.4</td>
<td>2.4</td>
</tr>
</tbody>
</table>

compared to other representative methods [1,30]: direct RPA on its own, second-order Møller-Plesset perturbation theory (MP2), SOSEX on its own, and coupled cluster with singles and doubles (CCSD). The basis set dependence of LC-$\omega$PBE+dRPA is lower than that of LC-$\omega$PBE+SOSEX for the $N_2$ dissociation energies, but is higher for the $N$ total energies.

Table 4.2 provides a summary of the basis set dependence of LC-$\omega$PBE+dRPA and
LC-\omega PBE+SOSEX for the atomization and barrier height energy test sets tested in this work. Calculations done with cc-pVTZ show a relatively small basis set dependence, with no calculation undergoing a change of more than approximately 0.9 kcal/mol. A larger basis set dependence is found for the larger G2-1 and NHTBH38/04 test sets as compared to the other test sets. The small basis set dependence of the AE6 set as opposed to the G2-1 set may be an artifact of the small size of the AE6 set, which does not include many of the first- and second-row elements that the G2-1 set does. On the other hand, the increase in MAE from the cc-pVTZ to the cc-pVQZ test set for the hydrogen transfer test sets (BH6 and HTBH38/04) shows that the error due to basis set incompleteness and the intrinsic error of the method cancel. However, the N and N$_2$ energy basis set dependence above suggests that the effect of increasing the basis set beyond cc-pVQZ should be relatively small, making results calculated using this basis set representative of the intrinsic performance of LC-\omega PBE+dRPA and LC-\omega PBE+SOSEX.
Table 4.2: Basis set dependence: Mean absolute errors (kcal/mol) in AE6 and G2-1 atomization energies, BH6 and HTBH38/04 hydrogen transfer barrier heights, and NHTBH38/04 non-hydrogen transfer barrier heights for the cc-pVTZ and cc-pVQZ basis sets. \( \text{LC-\( \omega \)PBE+dRPA} \) has \( \omega = 1.15, c_{\text{RPA}} = 1.63 \). \( \text{LC-\( \omega \)PBE+SOSEX} \) has \( \omega = 0.65, c_{\text{RPA}} = 1.63 \).
Chapter 5

Conclusion

When developing any new quantum chemistry method, three sometimes cooperative but often countervailing properties are generally sought after: accuracy, efficiency, and generality, both for types of systems and ease of extensibility. The functionals presented in this work are competitive on all three counts. Both LC-\(\omega\)PBE+dRPA and LC-\(\omega\)PBE+SOSEX show excellent accuracy on several types of calculations, and perform better than their predecessors LC-\(\omega\)LDA+dRPA and LC-\(\omega\)LDA+SOSEX. In addition, unlike many other forms of wave function correlation, RPA can be implemented to scale as \(O(N^5)\) in the number of orbitals, while the range separation can be used to ensure that RPA calculations are done only for the long range, where wave function methods are efficient. Meanwhile, the replacement of the range-separated LSDA functional with the range-separated PBE function demonstrates the overall robustness of the functional form—the results did not fluctuate wildly upon going from LSDA to PBE in the functionals, so it can be expected that further calculated improvements will increase the accuracy. Both the RPA and SR functional can easily be replaced by more accurate methods if desired.

The results presented here are evidence that both LC-\(\omega\)PBE+dRPA and LC-\(\omega\)PBE+SOSEX, when appropriately optimized for range separation and fraction of long-range correla-
tion, model both thermochemical phenomena and long-range weak interactions, as seen in noble gas dimers, to a very good degree; in particular, for thermochemical data, the functionals introduced in this work perform significantly better on the benchmarks than the previously optimized LC-ωLDA+dRPA and LC-ωLDA+SOSEX.

Just as for the LC-ωLDA-based functionals, it remains necessary to rescale the fraction of RPA correlation in the LC-ωPBE-based functionals such that $c_{\text{RPA}} > 1$, in fact increasing $c_{\text{RPA}}$ and $c_{\text{SOSEX}}$, which were optimized to 1.5 and 1.3 respectively, to 1.63 for both. On the other hand, the range-separation parameters hardly changed from LC-ωLDA+dRPA to LC-ωPBE+dRPA, decreasing from 1.2 to 1.15. The difference from LC-ωLDA+SOSEX to LC-ωPBE+SOSEX is more drastic, with the optimal $\omega$ for thermochemistry decreasing from 1.0 to 0.65. The decreased $\omega$ does allow for a slightly reduced calculation time due to the semilocal short-range, although the reduction in calculation time is on the order of 5%. Meanwhile, even optimized LC-ωPBE+SOSEX generally fares slightly worse than optimized LC-ωPBE+dRPA in the test sets presented here, although for charged particles, which were not tested here, LC-ωPBE+SOSEX may describe dissociation curves and total energies better than LC-ωPBE+dRPA, as is true for the LC-ωLDA-based functionals [1].

Despite the promising results of this functional, it is clear that more work remains to be done on RPA range-separated hybrids. The accuracy of LC-ωPBE+dRPA and LC-ωPBE+SOSEX might possibly be improved through the use of a new short-range functional, or even by optimizing it against a large test set than used in this
work. However, promising trends are appearing in the RPA literature [17], including the inclusion of single excitations along with RPA that may reduce the systematic underbinding of molecules seen with RPA [44], including in this work in section 4.2.
Bibliography


