
Ab-Initio Numerical Methods of Many-Body Quantum Systems and Applications to Superconducting Materials



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Abstract

Since the discovery of superconductivity by Onnes in 1911 [1] significant theoretical and experimental efforts have been devoted to the understanding of this phenomenon. Thanks to the Nobel Prize winning microscopic theory provided by Bardeen, Cooper and Schrieffer [3] we can understand conventional superconductivity as a many-body quantum mechanics problem consisting of a large number of mutually interacting electrons and nuclei. In the following we begin with a survey of ab-initio approaches to the many-electron problem, principally Hartree-Fock and Density Functional Theory. We then calculate the ground-state energies, equilibrium bond lengths and vibrational spectra for select molecules via custom computer code and compare with experimental values. We finish by outlining the generalization of Density Functional Theory into the superconducting state and discuss how the superconducting critical temperature can be calculated from such methods.

1 A Brief Introduction to Superconductivity

The phenomenon of superconductivity was discovered at the University of Leiden in 1911 by Dutch physicist Heike Kamerlingh Onnes in an experiment in which he observed the electrical resistivity of a mercury wire suddenly drop to zero when cooled below 4.2K [1] (See Figure 1).

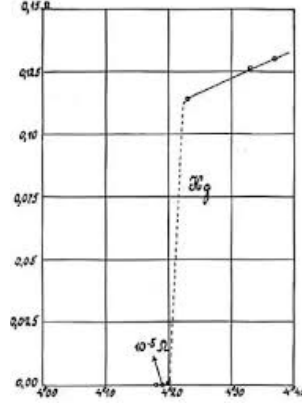


Figure 1: Onnes' famous plot showing the electrical resistivity of Mercury drop to zero at 4.2K [1].

By 1957 two important theories had provided a successful account, phenomenologically through Landau-Ginzburg theory [2] and microscopically through Bardeen-Cooper-Schrieffer (BCS) theory [3]. In the BCS account, below some critical temperature distortions of the lattice (phonons) allow electrons to form a Cooper pair state with boson like properties. The newly formed Cooper pairs can then condensate, whereby the energy to break the state is related to the energy to break all Cooper pairs. As such, at low temperatures charge can be transported in a material without resistance, hence - superconductivity.

In the context of BCS theory, conventional superconductivity is firmly grounded in many-body quantum mechanics. As famously stated by Dirac, due to the advent of the general theory of quantum mechanics:

...a large part of physics and the whole of chemistry are thus completely known and the difficulty is only that the exact applications of these laws leads to equations much too complicated to be soluble.[4]

Accordingly, much work has been focused on formulating appropriate methods of approximation to facilitate calculations of these problems.

Led by a desire to calculate the properties of superconducting materials ab-initio we conduct a brief survey and discussion of many-electron numerical methods, principally Hartree-Fock and Density Functional Theory (DFT), first dealing with the foundations of these theories in the normal state. We then present the results of custom computer code written to interact with implementations of said numerical methods and calculate the ground-state energies, equilibrium bond lengths and vibrational spectra of select atoms and diatomic molecules. We finish with a discussion of the generalization of DFT for the superconducting state (SCDFT) [24] and outline the approach to be used for calculating the properties of superconducting materials such as the phonon-electron coupling constant and critical temperature.

2 The Many-Electron Problem

In order to study the specific many-body problem posed by conventional superconductors we must start with the somewhat simpler case of approximation methods for electronic behaviour in solids. Firstly, we must consider the Hamiltonian of such a system of mutually interacting electrons and nuclei, which can be written as

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{en} + \hat{V}_{ee} + \hat{V}_{nn}, \quad (1)$$

where from left to right the terms are the kinetic energy of the electrons, the kinetic energy of the nuclei, the electron-nucleus attractive potential energy, the electron-electron repulsive potential energy and the nucleus-nucleus repulsive potential energy. The corresponding time independent Schrödinger equation is

$$\hat{H}\Psi(\mathbf{x}, \mathbf{R}) = E\Psi(\mathbf{x}, \mathbf{R}), \quad (2)$$

where \mathbf{x} denotes all electron positions and spins and \mathbf{R} denotes all nuclei positions. Indeed, equation (1) is completely general and solution of it would yield the energy of any system described as such. Unfortunately, it is not solveable and we will need to employ some approximations to obtain our desired quantities.

The first approximation we can make use of is the rigid lattice approximation, which allows us to neglect the kinetic energy of the nuclei and fix the nuclear-nuclear repulsion as a constant [5] due to the fact that the nuclear mass is significantly larger than the electronic mass. As a result, the Hamiltonian of the system reduces to

$$\hat{H}_e = \hat{T}_e + \hat{V}_{en} + \hat{V}_{ee}. \quad (3)$$

This yields an eigenvalue dependent only on the electrons:

$$\hat{H}_e\Psi(\mathbf{x}) = E\Psi(\mathbf{x}), \quad (4)$$

where, again, \mathbf{x} denotes the electron positions r_i and spins σ_i such that

$$\mathbf{x} = (\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N). \quad (5)$$

2.1 Hartree Theory

Following the historical account of events as presented in the textbook of Grosso and Parravicini [7], the first approach to solving this problem by Hartree was in 1927 [6], [7] in which he expressed the ground-state wavefunction of the system as a product of independent spin-orbitals

$$\Psi_0(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N) = \psi(\mathbf{r}_1\sigma_1)\psi(\mathbf{r}_2\sigma_2)\dots\psi(\mathbf{r}_N\sigma_N). \quad (6)$$

The spin-orbitals themselves a product of spatial orbitals $\phi_i(r)$ and the spin function $\chi_i(\sigma)$

$$\psi_i(r\sigma) = \phi_i(r)\chi_i(\sigma). \quad (7)$$

Hartree's method was to model the electron as travelling through an effective potential created by the attraction of all the nuclei in the system and the repulsion of all other electrons [8]. As a result, the Hamiltonian of the system is

$$\hat{H} = \hat{T}_e + \hat{V}_{eff}, \quad (8)$$

$$\hat{V}_{eff} = \hat{V}_{en} + \hat{V}_{coul}, \quad (9)$$

where \hat{T}_e is the total kinetic energy of the electrons and \hat{V}_{eff} the effective potential composed of the sum of attractive potential from the nuclei \hat{V}_{en} and the sum of repulsive potential from the other electrons \hat{V}_{ee} . From this we can define the *Hartree Potential*

$$V_{coul}(r) = \sum_j^{occ} \int \phi_j^*(r') \frac{e^2}{|r - r'|} \phi_j(r') dr', \quad (10)$$

which corresponds to an effective field experienced by an electron at \mathbf{r} , as a result of the charge distribution of the other electrons. By considering the electrons as independent and only interacting through this mean effective field the Hamiltonian is separable, and we obtain one-electron Schrödinger equations, known as the Hartree equations

$$[\hat{T}_e + \hat{V}_{eff}] \psi_i = \varepsilon_i \psi_i. \quad (11)$$

In order to solve these equations for the energies ε_i we must know the Hartree potential that is defined in terms of the occupied orbitals ϕ_j , which we do not know. To remedy this we solve self-consistently, meaning we make some reasonable guess of the occupied orbitals from which we can evaluate the charge distribution and Hartree Potential. From the solution we can obtain an improved set of wavefunctions, with the procedure repeated until no significant change is observed. In doing so we say we have solved self-consistently, which constitutes an important method required for numerical implementations of Hartree-Fock theory which shall be discussed in the forthcoming section.

In summary, Hartree theory provided a pioneering approach and a good footing for further methods, but itself failed to account for important aspects such as the fact that electrons will repel other electrons as they travel (electron correlation) and the requirement for the wavefunction to be antisymmetric as dictated by the Pauli exclusion principle. In the following decade Hartree, Slater and Fock worked to account for these shortcomings in the theory, eventually developing what is today known as Hartree-Fock theory.

2.2 Hartree-Fock Theory

Noting the requirement for antisymmetry the N-electron wavefunction was recast as a Hartree product, equation (6), with the addition of the antisymmetrizer operator

$$\mathcal{A} = \frac{1}{\sqrt{N!}} \sum_{i=1}^{N!} (-1)^{p_i} P_i, \quad (12)$$

which ensures the Pauli exclusion principle is satisfied. Thus for an N-electron system we find that a satisfactory wavefunction is constructed from a Slater determinant which can be expressed in the form [10]

$$\Psi = \frac{1}{\sqrt{N!}} \sum_i^{N!} (-1)^{P(i)} \psi_{i_1}(\mathbf{r}_1) \psi_{i_2}(\mathbf{r}_2) \dots \psi_{i_N}(\mathbf{r}_N). \quad (13)$$

Utilising the variational method we can obtain an approximation of the ground state for such a many-electron system using equation (13) as

$$E_{gs} \leq \langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle. \quad (14)$$

Thus by equations (8) and (9)

$$E_{gs} \leq \langle \Psi_0 | \hat{T}_e | \Psi_0 \rangle + \langle \Psi_0 | \hat{V}_{en} | \Psi_0 \rangle + \langle \Psi_0 | \hat{V}_{ee} | \Psi_0 \rangle, \quad (15)$$

where the kinetic energy and electronic-nuclear potential energy are dependent on the sum of one-electron operators and the Hartree Potential dependent on the sum of two-electron operators. Substitution of the ground state in determinantal form provides a functional to minimize according to the variational method

$$E_0 = \sum_i \langle \psi_i | \hat{T}_e + \hat{V}_{en} | \psi_i \rangle + \frac{1}{2} \sum_{ij}^N \left[\langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_j \psi_i \rangle \right]. \quad (16)$$

Using the spin-orbitals ψ_i as the variational parameter, E_0 can be minimised with the aid of Lagrange multipliers (see Appendix A) yielding the *Hartree-Fock equations*

$$\hat{F} \psi_i = \varepsilon_i \psi_i, \quad (17)$$

where we define the Fock operator

$$\hat{F} = \left[\hat{T}_e(\mathbf{r}) + \hat{V}_{en}(\mathbf{r}) + \hat{V}_{coul}(\mathbf{r}) + \hat{V}_{exch} \right]. \quad (18)$$

As a consequence of applying the variational method to the anti-symmetric Hartree product Ψ_0 , we are able to reduce the many-electron problem into a one-electron problem with the introduction of a new potential, the *Exchange Potential*

$$\hat{V}_{exch} = -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \langle \psi_i \psi_j | \frac{1}{\mathbf{r}_{ij}} | \psi_j \psi_i \rangle, \quad (19)$$

which is a quantum mechanical effect experienced between electrons of parallel spin. Again we obtain an eigenvalue which is a function of the occupied spin orbitals, which we do not know, and the self-consistent method provides a way forwards.

Taking the Hartree-Fock equations

$$\hat{F} |\psi_i\rangle = \varepsilon_i |\psi_i\rangle, \quad (20)$$

and multiplying both sides by $\langle \psi_i |$ we obtain an equation for the Hartree-Fock spin-orbital energies

$$\varepsilon_i = \langle \psi_i | \hat{F} | \psi_i \rangle. \quad (21)$$

By comparison with E_0 the Hartree-Fock ground state energy is

$$E_0^{(HF)} = \sum_i^{(occ)} \varepsilon_i - \frac{1}{2} \sum_{ij}^{occ} \left[\langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_j \psi_i \rangle \right]. \quad (22)$$

Addition of the nucleus-nucleus repulsive potential energy gives the total energy approximation under the Hartree-Fock treatment. As would be expected when utilising

the variational method, this is an overestimation of the exact ground state energy, the difference being the correlation energy mentioned in the previous section.

Hartree-Fock theory proved a significant improvement over Hartree's original approach, but importantly still neglects correlation in motion between electrons with anti-parallel spin. As a result, the method lacks accuracy in many systems and further methods of approximation were developed in response.

2.3 Using the Hartree-Fock method

To illustrate the use of the Hartree-Fock method we will restrict our discussion to closed-shell ground states. The total Hartree-Fock energy in this case is given by [12]

$$E_{tot}^{HF} = 2 \sum_{i=1}^{N/2} \langle \psi_i | T_e + V_{en} | \psi_i \rangle + \sum_i^{N/2} \sum_j^{N/2} \left[2 \langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_j \psi_i \rangle \right]. \quad (23)$$

In the case of Helium this is the sum of the first and second ionization energies and simplifies to

$$E_{tot}^{HF} = 2 \langle \psi_1 | T_e + V_{en} | \psi_1 \rangle + \langle \psi_1 \psi_1 | \frac{e^2}{r_{12}} | \psi_1 \psi_1 \rangle. \quad (24)$$

If we use the Gaussian ansatz [25]

$$\psi(r) = \left(\frac{2\alpha_{orb}}{\pi} \right)^{\frac{3}{4}} \exp(-\alpha_{orb} r^2), \quad (25)$$

we can obtain an expression for the total energy by Hartree-Fock (Appendix B) through substitution into equation (24), yeilding

$$E_{tot}^{HF} = 2 \left(\frac{3}{2} \alpha_{orb} - \sqrt{\frac{32}{\pi}} \alpha_{orb}^{1/2} \right) + \left(\frac{4}{\pi} \right)^{1/2} \alpha_{orb}^{1/2}. \quad (26)$$

Minimizing with respect to α_{orb} gives

$$E_{tot}^{HF} = -3.05 \text{ au}, \quad (27)$$

as compared to the established experimental value [13]

$$E_{tot}^{exp} = -2.90 \text{ au}. \quad (28)$$

Therefore, for a simple system such as Helium, Hartree-Fock theory yields reasonably accurate results despite neglecting electron correlation effects.

3 Density Functional Theory

In the previous sections we covered the foundations of the Hartree and Hartree-Fock approaches to the many-electron problem and illustrated their complexity for simple cases in the appendices. In the next section we discuss Density Functional Theory (DFT), a technique which has established itself as the dominant computational method for electronic structure calculations by changing the focus from the complexity of the 3N dimensional wavefunction, as with Hartree-Fock, to the much simpler three dimensional electronic density.

Consider the electronic Hamiltonian again

$$\hat{H}_e = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{en}, \quad (29)$$

and decompose into an internal part consisting of the total kinetic energy and electron-electron potential energy, and an external part consisting of the total electron-nucleus potential energy

$$\hat{H}_e = \hat{H}_{int} + \hat{V}_{ext}, \quad (30)$$

$$\hat{H}_{int} = \hat{T}_e + \hat{V}_{ee} = \sum_i \frac{\hat{\mathbf{p}}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (31)$$

$$\hat{V}_{ext} = \sum_i v_{ext}(\mathbf{r}_i) = - \sum_I \frac{z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|}. \quad (32)$$

where z_I is the nuclear charge and \mathbf{R}_I the position of nucleus I. The typical quantum mechanical approach would be to specify the system by choosing the external potential explicitly, but we can easily imagine how difficult this becomes in a system consisting of many electrons and nuclei. If we consider that the external potential corresponds to some field in which the electrons travel due to the configuration of the nuclei in the solid, and that the internal interactions are fixed, then the Hamiltonian of the system is dependent only on this external potential. The Hohenberg-Kohn theorem [15] tells us there is a one-to-one correspondence between this external potential and the ground-state density of the N-electron system, thus, by knowing this ground state density we know the Hamiltonian of the system and can avoid dealing with the many-body wavefunction. This approach was pioneered by Hohenberg and Kohn in their landmark 1964 paper [15], and allows highly accurate ground-state calculations for many-body systems without even considering the wavefunction, establishing itself as the dominant computational approach over the past 30 years [5].

To summarize Hohenberg and Kohn's logic, by defining the one-body ground-state density as

$$n(\mathbf{r}) = \langle \Psi_G(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) | \sum_i \delta(\mathbf{r} - \mathbf{r}_i) | \Psi_G(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \rangle. \quad (33)$$

then multiplying by v_{ext} and integrating over space we obtain

$$\begin{aligned} \int n(\mathbf{r}) v_{ext}(\mathbf{r}) d\mathbf{r} &= \langle \Psi_G(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) | \sum_i v_{ext}(\mathbf{r}_i) | \Psi_G(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \rangle \\ &= \langle \Psi_G(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) | V_{ext} | \Psi_G(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \rangle. \end{aligned} \quad (34)$$

Thus, there exists a functional linking the external potential to the electronic density e.g.

$$n(\mathbf{r}) = F[v_{ext}(\mathbf{r})]. \quad (35)$$

Importantly, Hohenberg and Kohn proved that this relationship can be inverted and there is a functional that links the electronic density to a unique external potential

$$v_{ext}(\mathbf{r}) = G[n(\mathbf{r})]. \quad (36)$$

Hence, through knowledge of the ground-state density we can determine any property of the ground-state system.

To summarize thus far, we have considered the Hamiltonian for a system in which the external potential energy is the variable of interest. Assuming we know this potential, we know the Hamiltonian and hence the ground-state wavefunction and its properties. Through the Hohenberg-Kohn theorem we then deduce that there is a one-to-one relationship between the external potential energy and the ground-state electronic density. As a result, all ground-state properties of the system are determined by the ground-state electronic density

$$v_{ext}(\mathbf{r}) \Rightarrow \Psi_G[v_{ext}] \Rightarrow E[v_{ext}], T[v_{ext}], V_{ee}[v_{ext}]. \quad (37)$$

From the Hohenberg-Kohn theorem

$$\Psi_G[n(\mathbf{r})] \Rightarrow E[n(\mathbf{r})], T[n(\mathbf{r})], V_{ee}[n(\mathbf{r})]. \quad (38)$$

Using this form and substituting into the variational method gives

$$E^{(HK)}[n(\mathbf{r}); v_{ext}(\mathbf{r})] \equiv \langle \Psi_G[n] | T + V_{ee} + V_{ext} | \Psi_G[n] \rangle, \quad (39)$$

and by expansion we obtain the Hohenberg-Kohn energy functional

$$E^{(HK)}[n(\mathbf{r}); v_{ext}(\mathbf{r})] \equiv T[n(\mathbf{r})] + V_{ee}[n(\mathbf{r})] + \int n(\mathbf{r})v_{ext}(\mathbf{r})d\mathbf{r}. \quad (40)$$

If we take the density as the variational parameter then the functional is minimized when $\Psi_G[n]$ is the exact ground-state, which corresponds to the exact ground-state electronic density. An important observation, and great news, is that $T[n(\mathbf{r})] + V_{ee}[n(\mathbf{r})]$ is a *universal* functional - it does not depend on the external potential $v_{ext}(\mathbf{r})$. Unfortunately however, the form of this functional is not known and is a major barrier in the application of DFT.

3.1 Kohn-Sham Equations

As prescribed by the variational method, we must minimize the energy functional, equation (40), we obtain with respect to the chosen variational parameter - in this case the ground-state electronic density. Since the Hohenberg-Kohn theorem applies to any system of electrons, not just the particular problem we address here, Kohn and Sham proposed to replace the many-electron problem with a system of non-interacting auxiliary electrons with the same ground-state density as the interacting one. As a result of the Hohenberg-Kohn theorem these two systems experience the same unique external potential $v_{ext}(r)$. We can now utilise a smart trick to “package” all of our unknowns together through reintroduction of the Hartree potential $V_H[n]$ and addition of the kinetic energy of the non-interacting particles $T_0[n]$:

$$\begin{aligned} E^{(HK)}[n(\mathbf{r}); v_{ext}(\mathbf{r})] &= T[n] + (T_0[n] - T_0[n]) + V_{ee}[n] + (V_H[n] - V_H[n]) \\ &\quad + \int n(\mathbf{r})v_{ext}(\mathbf{r})d\mathbf{r}. \end{aligned} \quad (41)$$

By simple rearrangement

$$E^{(HK)}[n(\mathbf{r}); v_{ext}(\mathbf{r})] = T_0[n] + V_H[n] + \int n(\mathbf{r})v_{ext}(\mathbf{r})d\mathbf{r} + E_{xc}[n], \quad (42)$$

with

$$E_{xc}[n] = T[n] - T_0[n] + V_{ee}[n] - V_H[n], \quad (43)$$

where $E_{xc}[n]$ is the exchange-correlation functional. If we then represent the ground-state density as a sum of independent orthonormal orbital contributions

$$n(\mathbf{r}) = \sum_i \phi_i^*(\mathbf{r})\phi_i(\mathbf{r}), \quad (44)$$

we find

$$E^{(HK)}[n(\mathbf{r}); v_{ext}(\mathbf{r})] = \sum_i \langle \phi_i | -\frac{\hbar^2 \hat{\nabla}^2}{2m} - v_{ext} | \phi_i \rangle + \sum_{ij} \langle \phi_i \phi_j | \frac{e^2}{r_{12}} | \phi_i \phi_j \rangle + E_{xc}[n]. \quad (45)$$

Using the variational method with the contributing orthonormal orbitals ϕ_i as the variational parameter, with the aid of Lagrange multipliers (Appendix A) we obtain the Kohn-Sham equations

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + V_{nucl}(\mathbf{r}) + V_{coul}(\mathbf{r}) + V_{xc}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}), \quad (46)$$

or more succinctly

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + V_{eff}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}), \quad (47)$$

where V_{eff} is not to be confused with that of equation (9). The total ground-state energy can be then expressed by

$$E_0 = \sum_i \varepsilon_i - \frac{1}{2} \sum_{ij} \langle \phi_i \phi_j | \frac{e^2}{r_{12}} | \phi_i \phi_j \rangle + E_{xc}[n] - \int V_{xc}(\mathbf{r})n(\mathbf{r})d\mathbf{r}. \quad (48)$$

The difficulty of the problem is now packaged up in the exchange-correlation energy functional $E_{xc}[n]$. Determining a reasonable approximation to this functional now becomes the main task, and once this is accomplished we can implement the method numerically.

3.2 Approximating the Exchange-Correlation Energy Functional

Making an appropriate approximation to the exchange-correlation energy functional is now the final step required for a practical implementation of DFT. The most common approach to this task is the local-density approximation (LDA) [9]. With an eye to progressing towards introducing Superconducting Density Functional Theory (SCDFT) we will not cover this approximation in depth, for it is not appropriate in the use of SCDFT. A short description, however, is included for completeness.

3.2.1 Local Density Approximation (LDA)

In the local density approximation the exchange-correlation functional is approximated as [16]

$$E_{xc}[n] = \int \varepsilon_{xc}(n(\mathbf{r}))n(\mathbf{r})d\mathbf{r}, \quad (49)$$

and the approach is to build the functional through approximation of the system as an homogeneous electron gas. Of course, this is only suitable in cases which the true electron density $n(\mathbf{r})$ is varying slowly.

In equation (49) above $\varepsilon_{xc}(n(\mathbf{r}))$ is the exchange-correlation energy per particle for the homogeneous electron gas, a uniform gas of interacting electrons, which can be calculated by use of Quantum Monte Carlo methods [17]. In such a system we imagine a positive charge of N , evenly smeared out in a cubic volume with N electrons, such that the total charge within the cube is zero. Since the positive charge is uniformly distributed the electrons maintain a uniform density and as such the attractive potential between the electrons and uniform positive charge exactly cancels the repulsive potential from electron-electron interactions. As a result, the total energy of the system is the total kinetic energy plus the exchange correlation energy. For such an approximation we find

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} = \varepsilon_{xc}(n(\mathbf{r})) + n(\mathbf{r}) \frac{d\varepsilon_{xc}(n(\mathbf{r}))}{dn(\mathbf{r})}, \quad (50)$$

which gives rise to an expression for the ground-state energy via substitution into equation (48)

$$E_0^{LDA} = \sum_i \varepsilon_i - \frac{1}{2} \int n(\mathbf{r}) \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}') d\mathbf{r} d\mathbf{r}' - \int n(\mathbf{r}) \left[\frac{d\varepsilon_{xc}}{dn} \right]_{n=n(\mathbf{r})}. \quad (51)$$

3.3 Using Density Functional Theory

Again, we can illustrate the use of the method via the Helium atom. The closed shell DFT equation of an N electron system is given by [12]

$$E_{tot}^{DFT} = 2 \sum_{i=1}^{N/2} \langle \psi_i | T_e + V_{en} | \psi_i \rangle + \sum_i^{N/2} \sum_j^{N/2} 2 \langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_i \psi_j \rangle - E_x. \quad (52)$$

In the case of Helium ($N=2$) this equation reduces to

$$E_{tot}^{DFT}(He) = 2 \langle \psi_1 | T_e + V_{en} | \psi_1 \rangle + 2 \langle \psi_1 \psi_1 | \frac{e^2}{r_{12}} | \psi_1 \psi_1 \rangle - E_x. \quad (53)$$

Here we can make use of the exchange-correlation functional as approximated in LDA given in equation (51)

$$E_{xc}[n] = \int \varepsilon_{xc}(n(\mathbf{r}))n(\mathbf{r})d\mathbf{r}. \quad (54)$$

Reusing the identical parts from the Hartree-Fock calculation we obtain a final ground-state energy (see Appendix C) of

$$E_{tot}^{DFT}(He) = -2.2008au. \quad (55)$$

The result above is in fact less accurate than that of the Hartree-Fock method, despite considering electron exchange and correlation effects. This is likely due to the crude approximation offered by LDA. As such, many more sophisticated approximations have been developed since the inception of DFT [18].

4 Numerical solutions to Hartree-Fock and DFT

Having now completed our survey of the theory required for ab-initio calculations of the properties of many-electron systems we progress to practical implementations of Hartree-Fock and DFT. By calculating analytical solutions of Hartree-Fock theory and DFT for the Helium atom in Appendices B and C we have illustrated the complexity of the many-electron problem even for the simplest systems. In the case of more complex systems analytical solutions do not in fact exist and we must resort to an efficient numerical method. To obtain said solutions we can employ NWChem [14], a high performance computational chemistry software package containing implementations of Hartree-Fock and DFT. In the following we will use these computational tools and develop custom code to present results for the ground-state energies, equilibrium bond lengths and vibrational spectra for select atoms and diatomic molecules.

4.1 Ground State Energy

For the few atoms for which it possible to experimentally determine the ground state energy we can consult the literature [21] for the values and compare against numerical solutions. If we construct the appropriate input file for a given atom and run NWChem we can implement both Hartree-Fock and DFT, yielding the following values:

| Element | Hartree-Fock | DFT (LDA) | Experimental |
|---------|--------------|-----------|--------------|
| He | -2.81 | -2.77 | -2.90 |
| Li | -7.31 | -7.22 | -7.48 |
| Ne | -126.60 | -126.15 | -128.94 |
| Ar | -521.22 | -520.19 | -527.60 |

Table 1: The ground state energies given in Hartrees (27.3eV) obtained using Hartree-Fock and DFT versus experimentally obtained values taken from Marder [21].

Interestingly, we see that Hartree-Fock produces more accurate results than DFT using the LDA exchange-correlation functional, likely due to the crude approximation offered by LDA.

4.2 Diatomic Molecule Bond Length

Although the ground-state energy for a diatomic molecule cannot be determined experimentally, other features dependent upon it are. For example, with the use of techniques such as X-Ray crystallography, it is possible to directly measure the bond length of a molecule.

To determine this bond length we can calculate numerical solutions for the diatomic ground-state energy using Hartree-Fock and DFT for a range of different nuclei separations. By writing a custom Python script (see Appendix D) to interact with NWChem we are able to automate the process of creating diatomic molecules for a range of nuclear separations, pass these files to NWChem for calculation of the total energy and then extract the values from the output files. The code then automatically plots the results and presents the bond length at which the energy of the molecule is minimised.

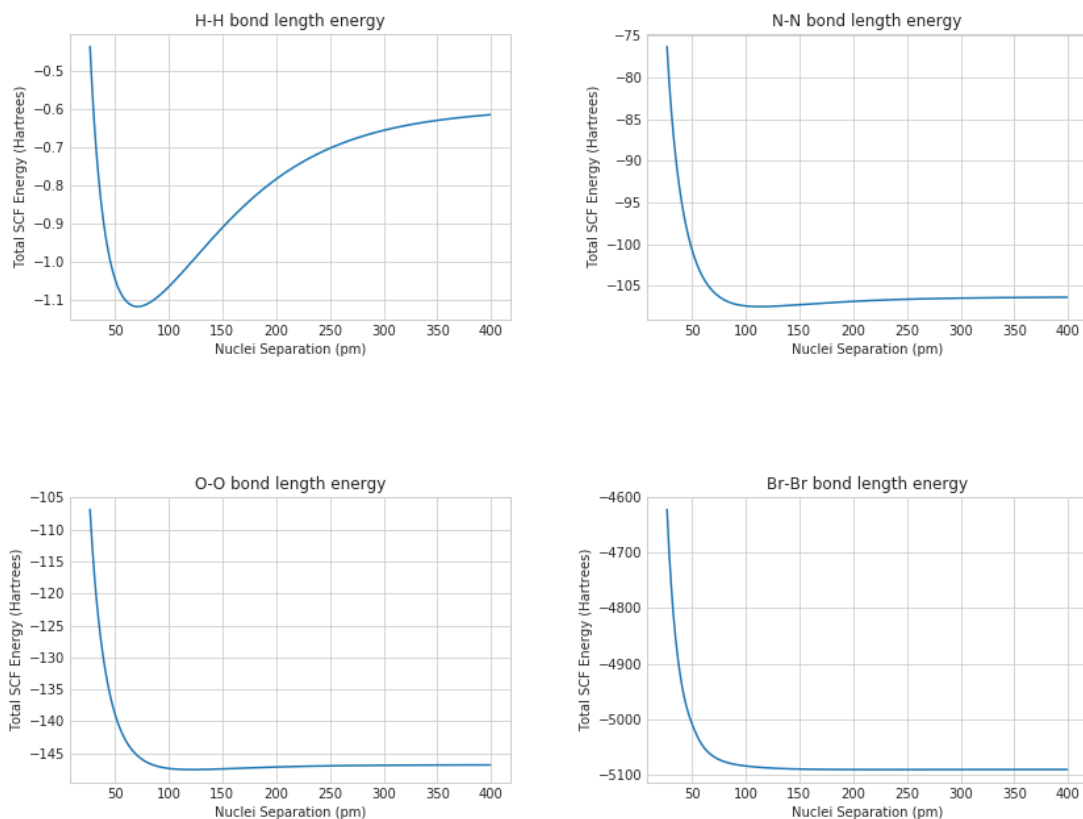


Figure 2: Plots of the total Hartree-Fock energy against bond length for diatomic H, N, O and Br obtained from the custom Python script (Appendix D).

We obtain very similar plots for the DFT calculation ¹, and can tabulate the bond lengths which minimize the energy calculated by each method

| Bond | Hartree-Fock | DFT (LDA) | Experimental |
|-------|--------------|-----------|--------------|
| H-H | 71.22 | 73.66 | 74.13 |
| N-N | 113.39 | 118.95 | 109.76 |
| O-O | 122.17 | 129.45 | 120.74 |
| Br-Br | 227.15 | 230.18 | 228.4 |

Table 2: Bond lengths (picometers) which minimize the total ground state energy as calculated by Hartree-Fock SCF and DFT (LDA). Experimental values taken from the Kaye & Laby Tables of Chemical & Physical constants [22].

Above we see some variation in the results with both Hartree-Fock SCF and DFT performing reasonably well.

4.3 Diatomic Molecule Vibrational Frequencies

Through calculating the energy of the diatomic molecule for a range of different nuclear separations as above in Figure 2 we now have a relationship for energy as a function of

¹These plots were excluded as they do not provide any information beyond the same plots for the Hartree-Fock SCF ones above

distance. If we model the diatomic molecule as a spring system then by Hooke’s law

$$F = -kx, \quad (56)$$

where k is the spring constant and x the nuclear separation. Since force is the first derivative of the energy U

$$F = -\frac{dU}{dx}, \quad (57)$$

we can obtain the spring constant of the diatomic molecule by

$$\frac{d^2U}{dx^2} = k. \quad (58)$$

Since the frequency and the spring constant are related by

$$\omega = \sqrt{\frac{k}{m}} \quad (59)$$

where for a diatomic molecule m is the reduced mass we can now relate the vibrational frequency to our energy plots (Figure 2). In order to calculate the vibrational frequencies of the diatomic molecules listed in Table 2 we could make an harmonic approximation around the bond length which minimizes the energy. Conveniently, however, NWChem provides functionality to calculate this for us. Through constructing the input files corresponding to the equilibrium bond length and specifying to NWChem to calculate the vibrational frequencies (Appendix E) we obtain

| Bond | Hartree-Fock | DFT (LDA) | Experimental |
|-------|--------------|-----------|--------------|
| H-H | 5481.7 | 4988.5 | 4401.2 |
| N-N | 2669.4 | 2159.0 | 2358.6 |
| O-O | 2065.5 | 1602.2 | 1580.2 |
| Br-Br | 435.9 | 388.3 | 325.3 |

Table 3: Vibrational frequencies ω in cm^{-1} . Experimental values taken from the NIST Computational Chemistry Comparison and Benchmark DataBase [23].

As a result, we see that both Hartree-Fock and DFT describe the behaviour around the equilibrium bond length well, as evidenced by reasonable calculations of the vibrational frequencies.

5 Superconducting Density Functional Theory

After covering the groundwork for regular Density Functional Theory in the sections above we can return to our original motivation, ab-initio calculations of the properties of superconducting materials, by reconsidering the physical picture depicted through BCS theory [3].

In order to generalize DFT for use in the superconducting state we must return to first principles. In Section 2, equation (3), we began by applying the rigid lattice approximation in which we neglected the kinetic energy of the nuclei and fixed the nuclear-nuclear repulsion as a constant. This is clearly not an appropriate approximation to make if we think back to the physics of superconductors as described by

BCS theory [3] - in which phonons, excitations of the nuclear lattice, are responsible for producing Cooper pairs. Thus, we must reformulate our Hamiltonian to reconsider interacting nuclei as before

$$\hat{H} = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{en} + \hat{T}_{nn} + \hat{V}_{nn} + \hat{H}_{ext}, \quad (60)$$

with the addition of some external field H_{ext} which is introduced to break the phase symmetry and allow a superconducting condensate to be formed [24] (a pairing of electrons into Cooper pairs to form a boson like condensate, see BCS theory for more [3]).

Initially formulated by Oliveira, Gross and Kohn [26], generalisation of DFT for the superconducting state requires introduction of three external fields, and by the Hohenberg-Kohn theorem, three densities [24]. Symmetry breaking in the system is achieved through coupling to an external superconductor which acts to tunnel Cooper pairs in and out, introducing Δ_{ext} , the proximity field. An external field coupling to the nuclei $W_{ext}\{\mathbf{R}_i\}$ is also introduced, allowing for construction of a non interacting system of nuclei which replicates phonons. In contrast to regular DFT, we now have the electronic density $\rho(\mathbf{r})$, the superconducting density $\chi(\mathbf{r}, \mathbf{r}')$ and the N-particle density matrix $\Gamma(\{\mathbf{R}_i\})$.

Following a similar procedure to that in the derivation of DFT, through the Hohenberg-Kohn theorem one can prove a one-to-one mapping between the densities and these external potentials. Likewise, we can apply the variational principle and determine that there exists a functional [24]

$$\Omega[\rho_0, \chi_0, \Gamma_0] = \Omega_0, \quad (61)$$

i.e. the grand canonical potential Ω_0 is determined uniquely by the ground state electronic density, superconducting density and N-particle density matrix. This follows the exact same logic as in equation (36) wherein we found the external potential as a functional of the ground state electronic density. We are once again in a position to move from a system with a one-to-one mapping between potentials and densities to a Kohn-Sham system of non-interacting superconducting electrons and interacting nuclei with the same ground-state density as the interacting one.

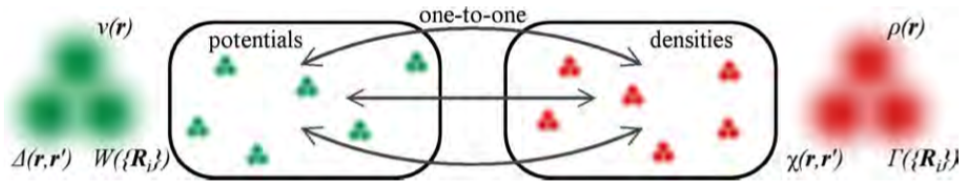


Figure 3: Diagram showing the one-to-one mapping between potentials and densities in SCDFT [24]

From this one can derive the SCDFT Kohn-Sham equations. Through connections to Eliashburg theory [27] we can determine some appropriate approximation to the exchange-correlation functional, enabling practical implementation of the method.

6 Final Remarks and Future Work

In the sections above we conducted a survey of ab-initio numerical methods for many-electron systems with an eye towards generalizing these approaches to the superconducting state. We followed an historical account first approaching the problem by approximating the many-electron wavefunction as done by Hartee, Fock, Slater and others in the early 1920s and 1930s. We then introduced the landmark work by Hohenberg and Kohn in which they proved that the complexity of the problem can be reduced from the 3N dimensional wavefunction to the 3 dimensional electronic density [15]. Through the Kohn-Sham equations we introduced the exchange-correlation energy functional and discussed methods of approximating it. We then used NWChem [14] and developed custom code to calculate the ground-state energies, equilibrium bond lengths and vibrational spectra of select atoms and diatomic molecules. Finally, we discussed how DFT can be generalized to account for superconductivity [24] with much of the same logic used in the development of regular DFT.

Due to time constraints it was not possible to implement a numerical solution of SCDFt to obtain the superconducting critical temperature of a material. We will however discuss the framework for doing so to illustrate how this can be achieved. To evaluate the transition temperature T_c of a material we can make use of approximations to the Eliashburg function in the form of the McMillan and Allen-Dynes formula [28]

$$T_c = \frac{\omega_{log}}{1.2} \exp \left(- \frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right), \quad (62)$$

where T_c is the critical temperature, ω_{log} the characteristic phonon frequency, λ the electron-phonon coupling constant and μ^* a pseudo Coulomb potential which is used as an empirical value. Using Quantum Espresso [30], an open-source suite of computer codes for electronic structure calculations, one can calculate λ , the electron-phonon coupling constant where

$$\lambda = 2 \int \frac{\alpha^2 F(\omega)}{\omega} d\omega. \quad (63)$$

Here $\alpha^2 F(\omega)$ is the Eliashberg spectral function which describes how the (Kohn-Sham) band structure is modified by the presence of phonons and can be expressed as

$$\alpha^2 F(\omega) = \frac{1}{N(0)} \sum_{n\mathbf{k}, m\mathbf{q}, v} |g_{n\mathbf{k}, m\mathbf{k}+\mathbf{q}}^v|^2 \delta(\xi_{n\mathbf{k}}) \delta(\xi_{n\mathbf{k}+\mathbf{q}}) \delta(\omega - \omega_{v\mathbf{q}}). \quad (64)$$

Above $N(0)$ is the density of states at the Fermi level, $\xi_{n\mathbf{k}}$ a one-particle band energy for band index n and wave vector \mathbf{k} , $\omega_{v\mathbf{q}}$ the phonon frequency at mode v and wavevector \mathbf{q} and $g_{n\mathbf{k}, m\mathbf{k}+\mathbf{q}}^v$ the electron-phonon coupling. Equation (64) can be evaluated by simply taking a discrete summation on finite \mathbf{k} and \mathbf{q} point meshes, but the convergence of the method is very slow as the size of the mesh must increase to accurately approximate the delta functions [29]. Upon doing so we can render an ab-initio calculation of the superconducting critical temperature T_c .

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ab-initio numerical methods and Dr. Bhaseen for allowing the degree of freedom he did in the direction of this project.

Appendix A Lagrange Multipliers

As seen in the Section 2.2, we employ the variational method to determine the ground-state energy of the multi-electron system which requires minimization of expression equation (15). If we are to follow Hartree's approach however, we must minimize the expression subject to the constraint that the spin-orbitals are independent and hence orthogonal.

A way to achieve this is through the method of Lagrangian multipliers, in which the general expression takes the form

$$\nabla f(x, y, z) = \varepsilon \nabla g(x, y, z), \quad (65)$$

where $f(x, y, z)$ is the function to be minimized, ε the Lagrange multiplier and $g(x, y, z)$ the function describing the constraint. Since it is the energy to be minimized with the constraint that we retain orthogonality, the constraint is

$$\sum_i \sum_j \langle \phi_i | \phi_j \rangle = \text{const.} \quad (66)$$

we can write

$$\nabla E = \sum_i \sum_j \varepsilon_{ij} \nabla \langle \psi_i | \psi_j \rangle, \quad (67)$$

tending to the left hand side of the equation

$$\nabla E = \nabla \left(\sum_i \langle \psi_i | T_e + V_{en} | \psi_i \rangle + \frac{1}{2} \sum_{ij}^N \left[\langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_j \psi_i \rangle \right] \right), \quad (68)$$

where we are varying the contributing spin-orbitals to minimize the energy. Tackling this term by term, to leading order we find

$$\nabla \langle \psi_i | \hat{T}_e + \hat{V}_{en} | \psi_i \rangle = \langle \delta \psi_i | \hat{T}_e + \hat{V}_{en} | \psi_i \rangle + \langle \psi_i | \hat{T}_e + \hat{V}_{en} | \delta \psi_i \rangle, \quad (69)$$

where we can consider the variations $\delta \psi_i$ and $\delta \psi_i^*$ independent. For a choice that $\delta \psi_i = 0$ we have

$$\nabla \langle \psi_i | \hat{T}_e + \hat{V}_{en} | \psi_i \rangle = \langle \delta \psi_i | \hat{T}_e + \hat{V}_{en} | \psi_i \rangle. \quad (70)$$

Applying the same technique gives

$$\nabla \left(\langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_j \psi_i \rangle \right) = \langle \delta \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_i \psi_j \rangle - \langle \delta \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_j \psi_i \rangle, \quad (71)$$

thus

$$\sum_i \langle \delta\psi_i | \hat{T}_e + \hat{V}_{en} | \psi_i \rangle + \frac{1}{2} \sum_{ij} \left[\langle \delta\psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_i \psi_j \rangle - \langle \delta\psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_j \psi_i \rangle \right] = \sum_{ij} \varepsilon_{ij} \langle \delta\psi_i | \psi_j \rangle, \quad (72)$$

which leads us to the Hartree-Fock equation found in Section 2.2.

Appendix B Hartree-Fock Calculation for the Helium atom

In Section 2.3 we illustrate the use of the Hartree-Fock theorem by analytical calculation for the Helium atom. Starting from the equation

$$E_{tot}^{HF} = 2\langle \psi_1 | T_e + V_{en} | \psi_1 \rangle + \langle \psi_1 \psi_1 | \frac{e^2}{r_{12}} | \psi_1 \psi_1 \rangle, \quad (73)$$

we can use atomic units and a Gaussian ansatz in the form [25]

$$\psi(r) = \left(\frac{2\alpha_{orb}}{\pi} \right)^{\frac{3}{4}} \exp(-\alpha_{orb} r^2). \quad (74)$$

If we break equation (73) into its respective parts and deal with them one by one, starting with the kinetic energy of the electrons we have:

$$\langle \psi_1 | T_e | \psi_1 \rangle = \langle \psi_1 | \frac{\nabla^2}{2} | \psi_1 \rangle. \quad (75)$$

We can substitute a Laplacian into the equation above in the following form, as the ansatz is dependent only on the radial coordinate:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right). \quad (76)$$

Substituting this into equation (75) yields

$$\langle \psi_1 | T_e | \psi_1 \rangle = \frac{4\pi}{2} \int_0^\infty \psi_1^* \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi_1}{\partial r} \right) dr. \quad (77)$$

Equation (77) can be solved with the aid of the following integral

$$\int_0^\infty x^n e^{-ax^2} dx = \frac{\Gamma(\frac{n+1}{2})}{2a^{\frac{n+1}{2}}} \quad (n > -1, a > 0). \quad (78)$$

and doing so yields the value

$$\langle \psi_1 | T_e | \psi_1 \rangle = -\frac{3}{2} \alpha_{orb}. \quad (79)$$

In the same vein,

$$\begin{aligned} \langle \psi_1 | V_{en} | \psi_1 \rangle &= 4\pi \left(\frac{2\alpha}{\pi} \right)^{3/2} \int_0^\infty r \exp(-2\alpha r^2) dr \\ &= -\sqrt{\frac{32}{\pi}} \alpha_{orb}^{1/2}. \end{aligned} \quad (80)$$

And finally, addressing the final term of equation (73)

$$\langle \psi_1 \psi_1 | \frac{1}{r_{12}} | \psi_1 \psi_1 \rangle = \left(\frac{2\alpha}{\pi} \right)^3 \int_0^\infty \frac{\exp(-2\alpha(r_1^2 + r_2^2))}{\sqrt{r_1^2 - r_2^2 - 2r_1 r_2 \cos \theta}} d\mathbf{r}_1 d\mathbf{r}_2. \quad (81)$$

If we set one electron along the z-axis and make the substitution $u = \cos \theta_1$ then by the following calculation

$$\int_0^\pi \int_0^\infty \frac{r_1^2 \exp(-2\alpha r_1^2)}{\sqrt{r_1^2 - r_2^2 - 2r_1 r_2 \cos \theta}} dr_1 d\theta_1 = \int_{-1}^1 \int_0^\infty \frac{r_1^2 \exp(-2\alpha r_1^2)}{\sqrt{r_1^2 - r_2^2 - 2r_1 r_2 u}} dr_1 du \quad (82)$$

$$\begin{aligned} &= 2 \left(\frac{1}{r_2} \int_0^{r_2} \exp(-2\alpha r_1^2) r_1^2 dr_1 + \int_{r_2}^\infty \exp(-2\alpha r_1^2) r_1 dr_1 \right) \\ &= 2 \left(\frac{\exp(-2\alpha r_2^2)}{8\alpha} + r_2 \right), \end{aligned} \quad (83)$$

we obtain a result of

$$\begin{aligned} \langle \psi_1 \psi_1 | \frac{1}{r_{12}} | \psi_1 \psi_1 \rangle &= \frac{64\alpha^3}{\pi} \int_0^\infty \exp(-4\alpha r_2^2) \left(\frac{\exp(-4\alpha r_2^2)}{8\alpha} + r_2 \right) r_2^2 dr_2 \\ &= \frac{32\alpha^3}{\pi^2} \frac{1}{8\alpha} = \frac{4\alpha_{orb}^2}{\pi^2}. \end{aligned} \quad (84)$$

NOTE: We encountered a problem with the calculation in equation (84) which we were not able to reconcile in the given time. We believe this was due to some abuse of notation in the textbook/paper we were using as reference [25] [12]. As such, we take the result from [25]:

$$\langle \psi_1 \psi_1 | \frac{1}{r_{12}} | \psi_1 \psi_1 \rangle = \left(\frac{4}{\pi} \right)^{\frac{1}{2}} \alpha_{orb}^{\frac{1}{2}} \quad (85)$$

Appendix C DFT Calculation for the Helium atom

In this appendix we elaborate on Section 3.3 and illustrate the use of DFT by analytical calculation of the Helium atom. Starting with equation (53)

$$E_{tot}^{DFT}(He) = 2\langle \psi_1 | T_e + V_{en} | \psi_1 \rangle + 2\langle \psi_1 \psi_1 | \frac{e^2}{r_{12}} | \psi_1 \psi_1 \rangle - E_x, \quad (86)$$

we can make use of our local density approximation $E_{xc}[n]$ from equation (49)

$$E_{xc}[n] = \int \varepsilon_{xc}(n(\mathbf{r})) n(\mathbf{r}) d\mathbf{r}. \quad (87)$$

Furthermore, we can make use of the exchange energy per electron ε_{xc}^{HEG} calculated by both Dirac [19] and Bloch [20] for the homogeneous electron gas:

$$\varepsilon_{xc}^{HEG}[n(r)] = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} (n(r))^{1/3}. \quad (88)$$

Substituting both into equation (85) gives

$$E_{xc}[n] = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} (4\pi) \int_0^\infty r^2 n(r)^{4/3} dr. \quad (89)$$

We can represent the density as the square modulus of $\psi(r)$ over N ($N=2$ for Helium) such that

$$n(r) = \frac{1}{2} \left(\frac{2\alpha_{orb}}{\pi} \right)^{\frac{3}{2}} \exp(-2\alpha_{orb}r^2). \quad (90)$$

Making one final substitution into equation (88) yields the final expression, a known definite integral solvable through the integral given in equation (78)

$$E_{xc}[n] = -3\pi \left(\frac{3}{\pi} \right)^{\frac{1}{3}} \left(\frac{1}{2} \right)^{\frac{4}{3}} \left(\frac{2\alpha}{\pi} \right)^2 \int_0^\infty r^2 \exp\left(-\frac{8}{3}\alpha r^2\right) dr, \quad (91)$$

$$E_{xc}[n] \approx -0.15\alpha_{orb}^{\frac{1}{2}}. \quad (92)$$

Appendix D NWChem Python Script

In Section 4 we present the ground-state energy, the equilibrium bond length and the vibrational spectra for select atoms and diatomic molecules through use of NWChem and custom Python code written to interact with it. In this appendix we provide the code and a brief explanation. As a prerequisite NWChem must be correctly downloaded and installed as per the instructions (<http://www.nwchem-sw.org/index.php/Download>). The code below will take as input a list of desired elements and iterate through the specified nuclear separations, construct a NWChem input file for each, call NWChem using SCF or DFT and then log the total energy and nuclear separation. After completing the loop the code will then produce a plot of energy against separation and present the bond length for which the energy is minimized.

```
#import required packages
import os
import re
import numpy as np
import pandas as pd
import matplotlib.pyplot as plt
plt.style.use('seaborn-whitegrid')

#function which interacts with NWChem, specify the element
#to use for the diatomic molecule
def nwchem(elements):
    basis = 'sto-3g'
    charge = 0

    #loops through elements passed as argument
    for element in elements:
        separation = []
        energy = []
        name = element

        #creates .nw input files with separations between
        #27 and 400 picometers
```

```

for sep in np.arange(27,400,0.01):
    #appends separation to list
    separation.append(sep)
    #writes the .nw file for each element and separation
    with open(name + '.nw', 'w') as f:
        f.write('echo\n')
        f.write('start_' + name + '\n\n')
        f.write('permanent_dir_./perm\n')
        f.write('scratch_dir_./scratch\n\n')
        f.write('charge_' + str(charge) + '\n')
        f.write('geometry_units_picometers_noautosym\n')
        f.write(name+ '\t' +str(sep) + '\t0\t0\n')
        f.write(name+ '\t0\t0\t0\n')
        f.write('end\n\n')
        f.write('basis\n')
        f.write('_*_library_' + basis + '\n')
        f.write('end\n\n')
        f.write('dft\nend\n')
        f.write('task_dft\n')

    #command used to run nwchem and log output
    command = 'nwchem_' + name + '.nw>' + name + '.nwo'
    os.system(command)
    #extracts energy from output file
    with open(name+'.nwo', 'r') as f:
        for line in f:
            #change this from/to DFT/SCF for DFT or Hartree-Fock
            if re.match(r'^.*Total\sDFT\senergy\s=.\$', line):
                lineInfo = line.split()
                energy.append(float(lineInfo[-1]))

#construct dataframe of results
results_table = pd.DataFrame({"separations":separation,
                              "energy":energy})

#plot energy against separation
plt.plot(results_table['separations'],results_table['energy'])
plt.title(name+'_'+name+'_bond_length_energy')
plt.xlabel('Nuclei_Separation_(pm)')
plt.ylabel('Total_DFT_Energy_(Hartrees)')
print(results_table['separations'][results_table['energy'].idxmin()])
#save png image
plt.savefig(name+'.DFT.png')

```

Appendix E Obtaining Vibrational Frequencies in NWChem

E.1 Method 1: NWChem Task

We can use a subroutine within NWChem to calculate the vibrational frequency for us by passing it an input file with the equilibrium bond length for example:

```

echo
start H

permanent_dir ./perm

```

```

scratch_dir ./scratch

charge 0
geometry units picometers noautosym
H      73.66    0    0
H      0        0    0
end

basis
* library sto-3g
end

<dft/scf>
end

freq
temp 1 273
end

task <dft/scf> freq

```

where the task **freq** specifies to NWChem to calculate the vibrational frequency at the given molecule geometry. If we then run in the shell:

```
$ nwchem <file_name>.nw
```

we obtain the vibrational frequency as part of the output.

E.2 Method 2: Energy measurement fit

A more laborious way to achieve the same task is by fitting a polynomial to the energy data we obtained by varying the nuclear separation for the diatomic molecule. Since the spring constant can be found as the second derivative of the energy we can make an harmonic approximation around the equilibrium bond length and obtain the value.

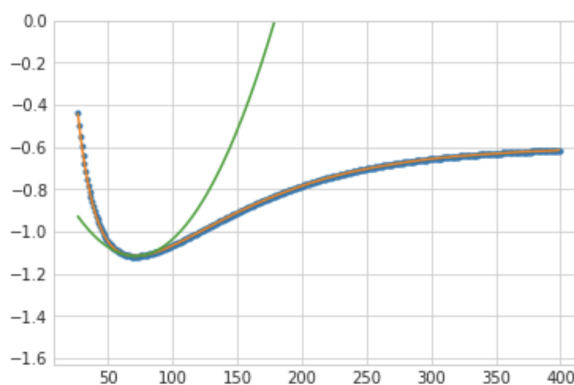


Figure 4: Harmonic approximation (green) for the Hartree-Fock Hydrogen energy spectra around the equilibrium bond length

Once an equation for the harmonic approximation has been obtained we can calculate k from its second derivative and then use equation (59) to calculate the vibrational frequency.

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