An Approach for the Correlation energy calculation of two-dimensional electron gas (2DEG) systems

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The problem of calculating correlation energy is relevant to all many-body physics system.The project is aimed at studying what correlation energy is and how it is calculated for many electron systems using different methods. These methods (approximations) will be tested using semi-analytic wave functions available for two electron systems.This work is motivated by a recent publication [1] where wigner crystallization (the zero temperature transition from a Fermi liquid to a quantum wigner crystal phase in monolayer transition metal dichalcogenides (TMDs)) is studied as an ideal example of the 2D system. The calculation made using different techniques both analytic and numerical, and results are compared with literature.

I. MANY ELECTRON SYSTEMS SIMPLEST MANY ELECTRON SYSTEM, HELIUM ATOM, USING PRINCIPLE OF VARIATION

The Hamiltonian for Helium atom is given by the following expression.

$$H = -\sum_{i=1,2}\left(\frac{1}{2}\nabla_i^2 + \frac{Z}{r_i}\right) + \frac{1}{|\vec{r}_1 - \vec{r}_2|} \tag{1}$$

To obtain an estimate function for the ground state, we neglect the r_{12} term and think of trial wave functions for the remaining Hamiltonian with a parameter to be varied. Minimizing the minimize the expectation of the Hamiltonian with respect to this parameter gives the value approximation to ground state energy.
If we take the wavefunction to be the product of hydrogen-like ground state wavefunctions.

$$\Psi(\vec{r}_1, \vec{r}_2) = \phi(\vec{r}_1)\,\phi(\vec{r}_2) \quad \text{where} \quad \phi(\vec{r}_1) = C_N e^{-ar} \tag{2}$$

The expectation of H comes of the form

$$\langle H\rangle = a^2 - 2Za + \frac{5a}{8} \tag{3}$$

On minimising, we get

$$\langle H\rangle_{\min} = -\left(Z - \frac{5}{16}\right)^2 \text{Ry} \approx -2.8476\text{Ry} \tag{4}$$

The experimental value being $-2.903693Ry$ [2] measured by extended two-photon Doppler-free spectroscopy to the vacuum ultraviolet spectral region. na

Next we take the wave function

$$\Psi(\vec{r}_1, \vec{r}_2) = C_N\left(e^{-ar_1 - br_2} + e^{-ar_2 - br_1}\right) \tag{5}$$

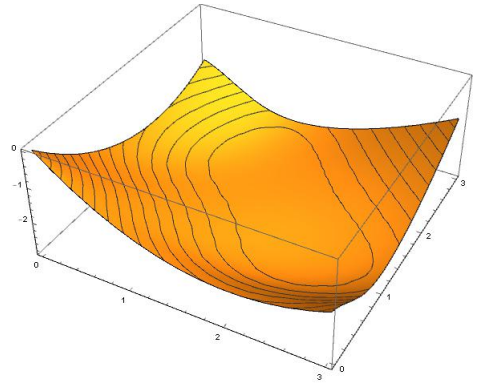

FIG. 1. Expectation Value of H for ψ in Eq.5

The energy is of the for this wavefunction is of the following form as a function of a and b

$$\begin{aligned}\langle H\rangle =& \frac{128a^4b^4 + (a+b)^6(a^2+b^2)}{2(64a^3b^3 + (a+b)^6} \\ &+ \frac{ab(a+b)(a^4 + 5a^3b + 28a^2b^2 + 5ab^3 + b^4)}{(a^2+6ab+b^2)(a^4 - 14a^2b^2 + b^4} \\ &+ Z(a+b)\end{aligned} \tag{6}$$

The expression is symmetric in a and b. On minimising for Z = 2 , we get

$$\langle H\rangle_{\min} \approx -2.8756\text{Ry} \tag{7}$$

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II. HOMOGENEOUS ELECTRON GAS (JELLIUM)

In real systems, ions with positive charge are positioned discretely. In the jellium model, we smear out the positive charge to get a uniform background potential.This allows us to study the interaction effects without the distracting and often inessential influence of the

periodic crystal potential. In d dimensions

$$\frac{(2\Pi)^d d}{2\Omega_d}\rho = (k_F)^d = (\frac{1}{\alpha_d r_s})^d \tag{8}$$

where r_s defines the average distance between electrons which is dimensionless because it in assumed to be multiplied by 1 a_B, Bohr radius, which is 1 in a.u., ρ the number density. When the density is high, at low values of r_s, the system behaves wave like, (also related to the Fermi Liquid). At low densities, the particle like behaviour surfaces, and the electrons form a crystal structure (Wigner Crystal).

$$\hat{H} = \sum_i \frac{\hat{p}_i^2}{2} + \frac{1}{2L^2}\sum_{\vec{q}\neq 0} v_q \left(\hat{n}_{-\vec{q}} n_{\vec{q}} - \hat{N}\right) \tag{9}$$

HEG is routinely used as a reference state in modern electronic structure calculations. Here we do, what is called the Thomas Fermi Approximation for HEG in 3D, to find the energy as a functional of the density ρ

A. Thomas Fermi Approximation

The TF theory works on the fact that an inhomogeneous electron liquid (because interactions) of slowly varying density is locally indistinguishable from a homogeneous one, provided that the variation of the density is negligible on the scale of the wavelength of the most energetic electrons.

$$T^{\mathrm{TF}}[n] = \frac{d}{2(d+2)}\int n(\vec{r})\, k_F(\vec{r})^2\, \mathrm{d}^d r \tag{10}$$

For $d = 2$, $T^{\mathrm{TF}} \propto \int \rho^2 d^2 r$ and $d = 3$, $T^{\mathrm{TF}} \propto \int \rho^{\frac{5}{3}} d^3 r$

The is well-known Thomas-Fermi kinetic energy functional, which is a functional of the local electron density. This can be applied to electrons in atoms as the local density approximation (LDA).

Taking the density to be $\rho(\vec{r}) = C_N e^{-ar}$ since density can be thought of as being proportional to the amplitude of the wavefunction, and minimizing with respect to a, we get $E_0 = -3.10229$Ry with 8.2% difference in Kinetic Energy term as compared to to when the electron wave function instead of density was taken to be Hydrogen-like.

We can improve on this in 3D by including the Weizsäcker gradient [3] correction

$$K_{\mathrm{W}}[\rho(\vec{r})] = \frac{1}{2\lambda}\int_{\mathbb{R}^3}\left(\vec{\nabla}\rho^{1/2}\right)^2 \mathrm{d}^3 r \tag{11}$$

Including the gradient correction, we get $E_0 = -2.7631$Ry which has lesser error. These calculation sgive us a faie idea of how good this approximation is in physical systems.

III. SLATER DETERMINANT

The wavefunction of electrons is completely antisymmetric in exchange of particles. Let $\psi_1, \ldots, \psi_N$ be an arbitrary orthonormal collection of one-particle states. We antisymmetrise by

$$\Psi(\vec{r}_1, \ldots, \vec{r}_n) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_1(\vec{r}_1) & \cdots & \psi_N(\vec{r}_N) \\ \vdots & \ddots & \vdots \\ \psi_1(\vec{r}_1) & \cdots & \psi_N(\vec{r}_N) \end{vmatrix} \tag{12}$$

The Slater wavefunction ignores electron interactions; i.e., the N-electron probability distribution factors into a product of N one-electron distributions.The column index runs over the labels ofthe occupied states, (j = 1,..,N) and the row index over the particleslabels (i = 1,..,N).It is evident from this representation of the wavefunction that any attempt to put more than one electron in the same state will give the null wave function the determinant of a matrix with two identical rows being zero.

IV. HARTREE-FOCK

Every hamiltonian can be written as

$$\hat{H} = \sum_i \hat{h}_1(\vec{x}_1) + \frac{1}{2}\sum_{i\neq j}\hat{h}_2(\vec{x}_i, \vec{x}_j) \tag{13}$$

The Hartree-Fock method is a variational, wavefunction-based approach. Although it is a many-body technique, the approach followed is that of a single-particle picture, i.e. the electrons are considered as occupying single-particle orbitals making up the wavefunction. Each electron feels the presence of the other electrons indirectly through an effective potential. Each orbital, thus, is affected by the presence of electrons in other orbitals. The starting point of the Hartree-Fock method is to write a variational wavefunction, which is built from these single particle orbitals. We shall use the slater determinant wavefunctions we defined in the previous section. The expectation value for the hamilonian for the wavefunction Ψ comes out to be the following, with the second intercation term having two components, the direct and exchange. [4]

$$\begin{aligned}\langle\Psi\left|\hat{H}_e\right|\Psi\rangle =& \sum_i^N \langle\psi\left|\hat{h}_1\right|\psi\rangle \\ &+ \frac{1}{2}\sum_{i\neq j}^N\left[\langle\psi_i\psi_j\left|\hat{h}_2\right|\psi_i\psi_j\rangle - \langle\psi_j\psi_i\left|\hat{h}_2\right|\psi_i\psi_j\rangle\right]\end{aligned} \tag{14}$$

The Hamiltonian when written for coulomb interaction

in d dimensions comes out to be the following,

$$\langle H\rangle_{\Psi} = \sum_i \int_{\mathbb{R}^d} \mathrm{d}^d r\ \psi_i^*(r)\left(-\frac{1}{2}\nabla^2 - \sum_{I\in\text{ions}}\frac{Z_I}{|\vec{r}-\vec{r}_I|}\right)\psi_i(r) + \frac{1}{2}\sum_{i,j}\int_{\mathbb{R}^{2d}} \mathrm{d}^d r \mathrm{d}^d r'\ \frac{\psi_i^*(\vec{r})\,\psi_j^*(\vec{r}')}{|\vec{r}-\vec{r}'|}\psi_i(\vec{r})\,\psi_j(\vec{r}') - \frac{1}{2}\sum_{i,j}\int_{\mathbb{R}^{2d}} \mathrm{d}^d r \mathrm{d}^d r'\ \frac{\psi_i^*(\vec{r})\,\psi_j^*(\vec{r}')}{|\vec{r}-\vec{r}'|}\psi_i(\vec{r}')\,\psi_j(\vec{r}) \tag{15}$$

A. Hartree-Fock ground state energy Calculation for 2D HEG

When the periodic potential is zero (or constant), the Hartree Fock equation can be solved exactly by choosing the ψ_i to be a set of orthonormal plane waves. [5]

$$\psi_i = \frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{L^d}} \tag{16}$$

In HEG, we have a uniform distribution of the positive charge, with same density as the electron density to have a neutral system. Hence, the potential of the ions is exactly cancelled by the direct interaction term of the electrons. Only the kinetic energy term and the exchange term survives. We evaluate the exchange term which is evaluated by writing the Coulomb interaction in terms of its Fourier Transform, which in 2D is $\frac{2\Pi}{|\vec{k}-\vec{q}|}$.

$$\frac{E_{HF}}{N} = \epsilon_0(r_s) + \epsilon_x(r_s) \tag{17}$$

where ϵ_0 is the direct non interacting kinetic energy and ϵ_x is exchange contribution. We define a new variable x where

$$x = \frac{|\vec{k}|}{|\vec{k}_F|}$$

. Since we are calculating the ground state energy at 0K, only states occupied are the ones within the Fermi sphere.

$$\epsilon_x = \frac{1}{2}\int_{-\infty}^{\infty} \epsilon_x^{\vec{k}}\,\mathrm{d}\vec{k} \tag{18}$$

$$\epsilon_x^{\vec{k}} = \begin{cases} -\frac{2\sqrt{2}E(x)}{\pi r_s} & x<1 \\ -\frac{2\sqrt{2}x\left(E\left(\frac{1}{x}\right)-\left(1-\frac{1}{x^2}\right)K\left(\frac{1}{x}\right)\right)}{\pi r_s} & x>1 \end{cases} \tag{19}$$

where $x = \frac{k}{k_F}$ and $E(x)$ and $K(x)$ are the complete elliptic integrals respectively of the first and second kind.

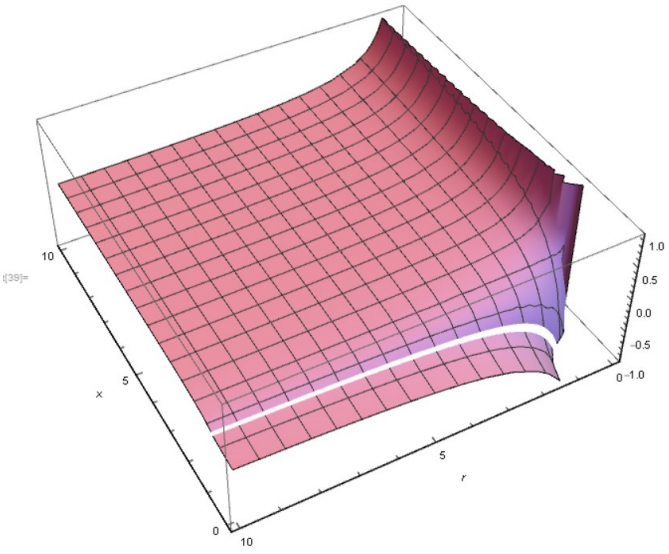

FIG. 2. Exchange energy as a function of r_s and $x = \frac{\vec{k}}{k_F}$

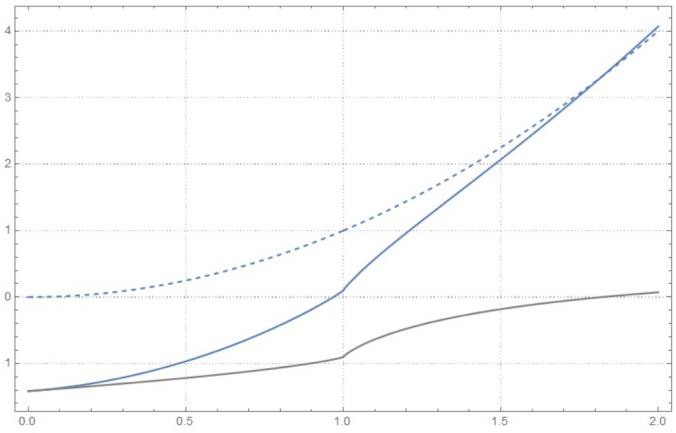

FIG. 3. Momentum dependence of the single particle energy $\epsilon^{HF}(\vec{k})$ in HF theory for a homogeneous two dimensional electron gas (full blue line). The grey line is the exchange contribution. The dotted line represents the non-interacting kinetic energy. Here $r_s = 2$.

On Integrating this inside the Fermi sphere we get the following:

$$\epsilon_x^{HF} = \frac{4\sqrt{2}}{3\pi r_s} = \frac{1.200}{r_s}Ry \tag{20}$$

$$\epsilon_0^{HF} = \frac{1}{r_s^2}Ry \tag{21}$$

B. Correlation

The approximate nature of the HF ground-states naturally leads to the concept of correlation. Correlation

effects are, by definition, all the effects that stem from the fact that the true ground-state wave function is not a single Slater determinant. The difference between the exact ground-state energy and the HF ground-state energy defines the correlation energy. Strictly speaking even a single Slater determinant is a correlated wave function due to its anti-symmetric structure. However, the word correlation is normally reserved only for those correlations that go beyond the inevitable anti-symmetry-related ones.

To find the correlation energy, we find do linear response theory, leading to RPA, the Random Phase Approximation discussed in the next section, we estimate energy and subtract the Hartree Fock terms to get the Correlation energy.

V. RPA

The best known and most successful approximation in the first class is the time-dependent Hartree approximation, universally known (for historical reasons) as the random phase approximation (RPA). In this theory one assumes that the electrons respond to the external field. Instead of calculating the interaction energy directly we study the first order response of the system (linear perturbation) to an external potential of the same form as that of the internal interaction. The density response function is calculated, in terms of the Linhard function.On further analysis, the final form of the correlation energy comes out to be the following,

$$\frac{\epsilon_C^{\mathrm{RPA}}}{\mathrm{Ry}} = -\frac{d}{2\alpha_d^2\pi r_s^2}\int_0^\infty \mathrm{d}y\, y^d \int_0^\infty \mathrm{d}\nu \left\{ \frac{\gamma_d}{y^{d-1}} f_d(y,\nu) - \log\left(1+\frac{\gamma_d}{y^{d-1}} f_d(y,\nu)\right)\right\} \tag{22}$$

where

$$f_d(y,\nu) = \frac{2\mathrm{Re}\,\Psi\left(\frac{y}{2}+i\nu\right)}{y} \tag{23}$$

and

$$\Psi_d(z) = \int_0^1 \mathrm{d}x\, x^{d-1} \int \frac{d\theta}{2\pi} \frac{1}{z - x\cos(\theta)} \tag{24}$$

A. High-Density Approximation

In this limit $r_s << 1$. We split the y integral into two parts, one up till y_c and one above it. We choose y_c such that $r_s << y_c << 1$. First, we need to evaluate

$$-\frac{d}{2\alpha_d^2\pi r_s^2}\int_0^{y_c} \mathrm{d}y\, y^d \int_0^\infty \mathrm{d}\nu \left\{ \frac{\gamma_d}{y^{d-1}} f_d(y,\nu) - \log\left(1+\frac{\gamma_d}{y^{d-1}} f_d(y,\nu)\right)\right\} \tag{25}$$

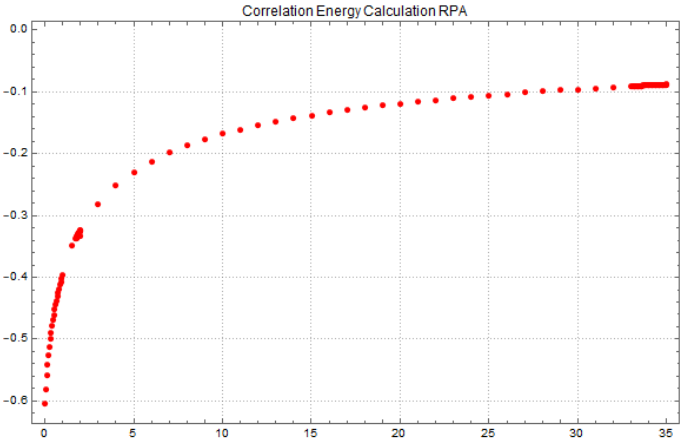

FIG. 4. Numerical $E_correlation$ in 2D HEG

$$= -\frac{d}{2\alpha_d^2\pi r_s^2}\int_0^\infty \mathrm{d}\nu \int_0^{y_c} \mathrm{d}y\, y^d \left\{ \frac{\gamma_d}{y^{d-1}} \Psi_d'(i\nu) - \log\left(1+\frac{\gamma_d}{y^{d-1}} \Psi_d'(i\nu)\right)\right\}$$

where the second form is justified by

$$\lim_{y\to 0} f_d(y,\nu) = \Psi_d'(i\nu) \tag{26}$$

which is real. This integral can be done analytically in 2D. The other part of the integral can be expanded to order γ_2^2 and then integrated by parts. Adding these two components, the singular part cancels so we can take the $y_c \to 0$ limit.[6] The final answer comes out to be

$$-A - B\, r_s \log r_s + O(r_s). \tag{27}$$

On fitting the data to the model, we obtain the following fit,

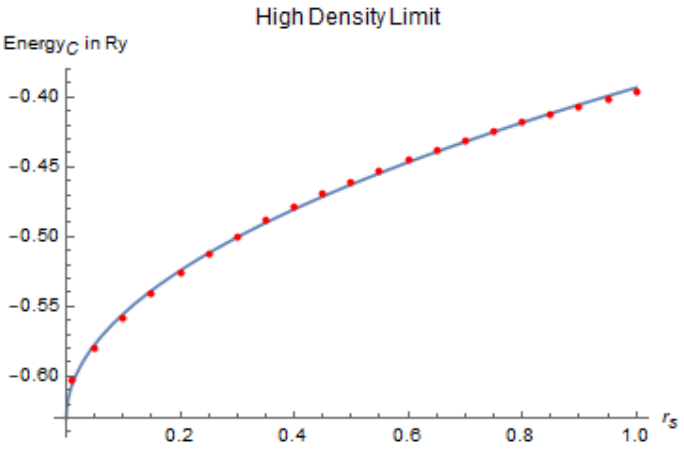

FIG. 5. Fit for the high density, low r_s

B. Low-Density Approximation

By taking $r_s \to \infty$ the radius of the Fermi sphere tends to 0. This situation is physically relevant only in the Wigner Crystal regime. In this limit, the correlation energy is proportional to $r_s^{-2/3}$. In the limit of infinite electronic species at a fixed total density, the RPA becomes exact.[7]. In the model fitting as $\frac{-a}{r_s^b}$ to our data, we obtain, $b = 0.55$ and $a = 0.62$. This limit is obtained for r_s values in the physical lower limit of density (Wigner Crystal domain).

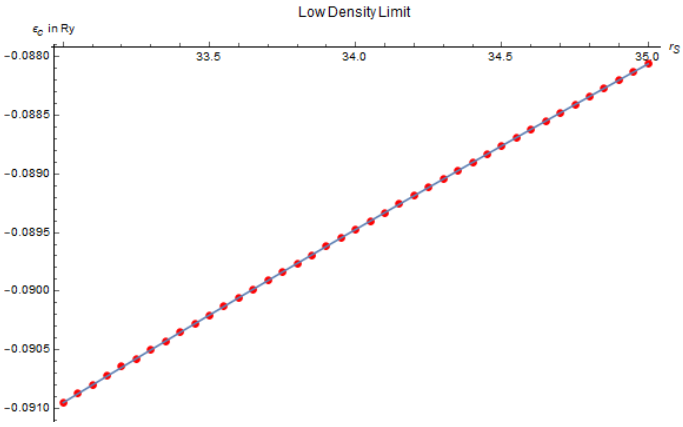

FIG. 6. Fit for the low density, high r_s, near Wigner Crystal Regime

Comparing to the standard 3D results [6] (also calculated for the project) e observe that kinetic energy in 2D is less than 3D, exchange energy is slightly larger, but the correlation energy in RPA is significantly higher in 2D.

VI. WIGNER CRYSTAL

A classical Wigner crystal is a collection of neutral BCC unit cells in 3D, and a close packed hexagonal structure in 2D such that each lattice point has its electron embedded in a uniform neutralizing background of a (sphere/disc).To determine the total energy, we represent each lattice site of the unit cell as a (sphere/disc) of radius r with the electron at its center. Let E be the electrostatic energy of a single unit cell consisting of the potential energy between the electron and the positive charged sphere E_e plus the self energy of the charged sphere.

The energy of a two dimensional Wigner crystal is approximately given by

$$\frac{U}{N} = -\frac{2.3}{r_s}\text{Ry} \tag{28}$$

The correlation energy calculation of the Wigner Crystal can be done by looking at the RPA low density approximation. In 2D, the Wigner Crystal like densities are found in Transition Metal Chalcogenides, like MoS_2.

VII. CONCLUSION

In this project, we tried to study many different ways to find the ground-state energy of a two dimensional electron gas. We used methods in order of increasing accuracy culminating in the RPA. We studied the RPA in the high and low density limits and also did numeric calculations to interpolate between them. The correlation energy calculated from the RPA and LDA can further be interpolated together to get better results.

[1] M. Zarenia, D. Neilson, B. Partoens, and F. M. Peeters. Wigner crystallization in transition metal dichalcogenides: A new approach to correlation energy. *Phys. Rev. B*, 95:115438, Mar 2017.

[2] S. D. Bergeson, A. Balakrishnan, K. G. H. Baldwin, T. B. Lucatorto, J. P. Marangos, T. J. McIlrath, T. R. O'Brian, S. L. Rolston, C. J. Sansonetti, Jesse Wen, N. Westbrook, C. H. Cheng, and E. E. Eyler. Measurement of the he ground state lamb shift via the two-photon $1^1s - 2^1s$ transition. *Phys. Rev. Lett.*, 80:3475–3478, Apr 1998.

[3] Weitao Yang. Gradient correction in thomas-fermi theory. *Phys. Rev. A*, 34:4575–4585, Dec 1986.

[4] Gabriele Giuliani and Giovanni Vignale. *Quantum Theory of the Electron Liquid*. Cambridge University Press, 2005.

[5] N.W. Ashcroft and N.D. Mermin. *Solid State Physics*. Saunders College, Philadelphia, 1976.

[6] Enrico Lipparini. *Modern Many-Particle Physics*. WORLD SCIENTIFIC, 2nd edition, 2008.

[7] C. Kittel. *Quantum Theory of Solids*. Wiley, 1987.