Homogeneous Electron gas

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The electron gas

The electron gas is perhaps the only realistic model of a system of many interacting particles that allows for a solution of the Hartree-Fock equations on a closed form. Furthermore, to first order in the interaction, one can also compute on a closed form the total energy and several other properties of a many-particle systems. The model gives a very good approximation to the properties of valence electrons in metals. The assumptions are

- System of electrons that is not influenced by external forces except by an attraction provided by a uniform background of ions. These ions give rise to a uniform background charge. The ions are stationary.
- The system as a whole is neutral.
- We assume we have N_e electrons in a cubic box of length L and volume $\Omega = L^3$. This volume contains also a uniform distribution of positive charge with density $N_e e/\Omega$.

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This is a homogeneous system and the one-particle wave functions are given by plane wave functions normalized to a volume Ω for a box with length L (the limit $L \to \infty$ is to be taken after we have computed various expectation values)

$$\psi_{\mathbf{k}\sigma}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \exp{(i\mathbf{kr})}\xi_\sigma$$

where $\mathbf{k}$ is the wave number and ξ_σ is a spin function for either spin up or down

$$\xi_{\sigma=+1/2} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \xi_{\sigma=-1/2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

We assume that we have periodic boundary conditions which limit the allowed wave numbers to

$$k_i = \frac{2\pi n_i}{L} \qquad i = x, y, z \qquad n_i = 0, \pm 1, \pm 2, \dots$$

We assume first that the electrons interact via a central, symmetric and translationally invariant interaction $V(r_{12})$ with $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. The interaction is spin independent. The total Hamiltonian consists then of kinetic and potential energy

$$\hat{H} = \hat{T} + \hat{V}.$$

The operator for the kinetic energy can be written as

$$\hat{T} = \sum_{\mathbf{k}\sigma} \frac{\hbar^2 k^2}{2m} a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma}.$$

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The Hamilton operator is given by

$$\hat{H} = \hat{H}_{el} + \hat{H}_b + \hat{H}_{el-b},$$

with the electronic part

$$\hat{H}_{el} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{e^2}{2} \sum_{i \neq j} \frac{e^{-\mu|\mathbf{r}_i - \mathbf{r}_j|}}{|\mathbf{r}_i - \mathbf{r}_j|},$$

where we have introduced an explicit convergence factor (the limit $\mu \to 0$ is performed after having calculated the various integrals). Correspondingly, we have

$$\hat{H}_b = \frac{e^2}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}') e^{-\mu|\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|},$$

which is the energy contribution from the positive background charge with density $n(\mathbf{r}) = N/\Omega$. Finally,

$$\hat{H}_{el-b} = -\frac{e^2}{2} \sum_{i=1}^{N} \int d\mathbf{r} \frac{n(\mathbf{r}) e^{-\mu|\mathbf{r} - \mathbf{x}_i|}}{|\mathbf{r} - \mathbf{x}_i|},$$

is the interaction between the electrons and the positive background.

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One can show that the Hartree-Fock energy can be written as

$$\varepsilon_k^{HF} = \frac{\hbar^2 k^2}{2m_e} - \frac{e^2}{\Omega^2} \sum_{k' \leq k_F} \int d\boldsymbol{r} e^{i(\boldsymbol{k'}-\boldsymbol{k})\boldsymbol{r}} \int d\boldsymbol{r'} \frac{e^{i(\boldsymbol{k}-\boldsymbol{k'})\boldsymbol{r'}}}{|\boldsymbol{r}-\boldsymbol{r'}|}$$

resulting in

$$\varepsilon_k^{HF} = \frac{\hbar^2 k^2}{2m_e} - \frac{e^2 k_F}{2\pi} \left[2 + \frac{k_F^2 - k^2}{k k_F} ln \left| \frac{k + k_F}{k - k_F} \right| \right]$$

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The energy can be rewritten in terms of the density

$$n = \frac{k_F^3}{3\pi^2} = \frac{3}{4\pi r_s^3},$$

where $n = N_e/\Omega$, N_e being the number of electrons, and r_s is the radius of a sphere which represents the volum per conducting electron. It is convenient to use the Bohr radius $a_0 = \hbar^2/e^2 m_e$. For most metals we have a relation $r_s/a_0 \sim 2 - 6$.

The electron gas, total energy

We have

$$\hat{H}_b = \frac{e^2}{2}\frac{N_e^2}{\Omega}\frac{4\pi}{\mu^2},$$

and

$$\hat{H}_{el-b} = -e^2\frac{N_e^2}{\Omega}\frac{4\pi}{\mu^2}.$$

The final Hamiltonian can be written as

$$H = H_0 + H_I,$$

with

$$H_0 = \sum_{\mathbf{k}\sigma}\frac{\hbar^2 k^2}{2m_e}a^\dagger_{\mathbf{k}\sigma}a_{\mathbf{k}\sigma},$$

and

$$H_I = \frac{e^2}{2\Omega}\sum_{\sigma_1\sigma_2}\sum_{\mathbf{q}\neq 0,\mathbf{k},\mathbf{p}}\frac{4\pi}{q^2}a^\dagger_{\mathbf{k}+\mathbf{q},\sigma_1}a^\dagger_{\mathbf{p}-\mathbf{q},\sigma_2}a_{\mathbf{p}\sigma_2}a_{\mathbf{k}\sigma_1}.$$

The electron gas, total energy

We can calculate $E_0/N_e = \langle\Phi_0|H|\Phi_0\rangle/N_e$ for for this system to first order in the interaction. Using

$$\rho = \frac{k_F^3}{3\pi^2} = \frac{3}{4\pi r_0^3},$$

with $\rho = N_e/\Omega$, r_0 being the radius of a sphere representing the volume an electron occupies and the Bohr radius $a_0 = \hbar^2/e^2 m$, that the energy per electron can be written as

$$E_0/N_e = \frac{e^2}{2a_0}\left[\frac{2.21}{r_s^2} - \frac{0.916}{r_s}\right].$$

Here we have defined $r_s = r_0/a_0$ to be a dimensionless quantity.

The electron gas, total energy

We can calculate the following part of the Hamiltonian using a convergence factor

$$\hat{H}_b = \frac{e^2}{2} \iint \frac{n(\boldsymbol{r})n(\boldsymbol{r}')e^{-\mu|\boldsymbol{r}-\boldsymbol{r}'|}}{|\boldsymbol{r}-\boldsymbol{r}'|} \, \mathrm{d}^3\boldsymbol{r} \, \mathrm{d}^3\boldsymbol{r}',$$

where $n(\boldsymbol{r}) = N_e/\Omega$, the density of the positive backgroun charge. We define $\boldsymbol{r}_{12} = \boldsymbol{r} - \boldsymbol{r}'$, reulting in $\mathrm{d}^3\boldsymbol{r}_{12} = \mathrm{d}^3 r$, and allowing us to rewrite the integral as

$$\hat{H}_b = \frac{e^2 N_e^2}{2\Omega^2} \iint \frac{e^{-\mu|\boldsymbol{r}_{12}|}}{|\boldsymbol{r}_{12}|} \, \mathrm{d}^3\boldsymbol{r}_{12} \, \mathrm{d}^3\boldsymbol{r}' = \frac{e^2 N_e^2}{2\Omega} \int \frac{e^{-\mu|\boldsymbol{r}_{12}|}}{|\boldsymbol{r}_{12}|} \, \mathrm{d}^3\boldsymbol{r}_{12}.$$

Here we have used that $\int \mathrm{d}^3\boldsymbol{r} = \Omega$. We change to spherical coordinates and the lack of angle dependencies yields a factor 4π, resulting in

$$\hat{H}_b = \frac{4\pi e^2 N_e^2}{2\Omega} \int_0^\infty r e^{-\mu r} \, \mathrm{d}r.$$

The electron gas, total energy

Solving by partial integration

$$\int_0^\infty r e^{-\mu r}\,\mathrm{d}r = \left[-\frac{r}{\mu}e^{-\mu r}\right]_0^\infty + \frac{1}{\mu}\int_0^\infty e^{-\mu r}\,\mathrm{d}r = \frac{1}{\mu}\left[-\frac{1}{\mu}e^{-\mu r}\right]_0^\infty = \frac{1}{\mu^2},$$

gives

$$\hat{H}_b = \frac{e^2}{2}\frac{N_e^2}{\Omega}\frac{4\pi}{\mu^2}.$$

The next term is

$$\hat{H}_{el-b} = -e^2\sum_{i=1}^{N}\int \frac{n(\boldsymbol{r})e^{-\mu|\boldsymbol{r}-\boldsymbol{x}_i|}}{|\boldsymbol{r}-\boldsymbol{x}_i|}\,\mathrm{d}^3\boldsymbol{r}.$$

Inserting $n(\boldsymbol{r})$ and changing variables in the same way as in the previous integral $\boldsymbol{y} = \boldsymbol{r} - \boldsymbol{x}_i$, we get $\mathrm{d}^3\boldsymbol{y} = \mathrm{d}^3\boldsymbol{r}$. This gives

$$\hat{H}_{el-b} = -\frac{e^2 N_e}{\Omega}\sum_{i=1^N}\int \frac{e^{-\mu|\boldsymbol{y}|}}{|\boldsymbol{y}|}\,\mathrm{d}^3\boldsymbol{y} = -\frac{4\pi e^2 N_e}{\Omega}\sum_{i=1}^{N}\int_0^\infty y e^{-\mu y}\mathrm{d}y.$$

The answer is

$$\hat{H}_{el-b} = -\frac{4\pi e^2 N_e}{\Omega}\sum_{i=1}^{N}\frac{1}{\mu^2},$$

which gives

$$\hat{H}_{el-b} = -e^2\frac{N_e^2}{\Omega}\frac{4\pi}{\mu^2}.$$

The electron gas, total energy

Finally, we need to evaluate $\hat{H}_{el}$. This term reads

$$\hat{H}_{el} = \sum_{i=1}^{N_e} \frac{\hat{\boldsymbol{p}}_i^2}{2m_e} + \frac{e^2}{2} \sum_{i \neq j} \frac{e^{-\mu|\boldsymbol{r}_i - \boldsymbol{r}_j|}}{\boldsymbol{r}_i - \boldsymbol{r}_j}.$$

The last term represents the repulsion between two electrons. It is a central symmetric interaction and is translationally invariant. The potential is given by the expression

$$v(|\boldsymbol{r}|) = e^2 \frac{e^{\mu|\boldsymbol{r}|}}{|\boldsymbol{r}|},.$$

The results becomes

$$\int v(|\boldsymbol{r}|)e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}\,\mathrm{d}^3\boldsymbol{r} = e^2\int \frac{e^{\mu|\boldsymbol{r}|}}{|\boldsymbol{r}|}e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}\,\mathrm{d}^3\boldsymbol{r} = e^2\frac{4\pi}{\mu^2+q^2},$$

which gives us

$$\begin{aligned}\hat{H}_{el} &= \sum_{\boldsymbol{k}\sigma}\frac{\hbar^2k^2}{2m}\hat{a}^\dagger_{\boldsymbol{k}\sigma}\hat{a}_{\boldsymbol{k}\sigma} + \frac{e^2}{2\Omega}\sum_{\sigma\sigma'}\sum_{\boldsymbol{kpq}}\frac{4\pi}{\mu^2+q^2}\hat{a}^\dagger_{\boldsymbol{k}+\boldsymbol{q},\sigma}\hat{a}^\dagger_{\boldsymbol{p}-\boldsymbol{q},\sigma'}\hat{a}_{\boldsymbol{p}\sigma'}\hat{a}_{\boldsymbol{k}\sigma} \\ &= \sum_{\boldsymbol{k}\sigma}\frac{\hbar^2k^2}{2m_e}\hat{a}^\dagger_{\boldsymbol{k}\sigma}\hat{a}_{\boldsymbol{k}\sigma} + \frac{e^2}{2\Omega}\sum_{\sigma\sigma'}\sum_{\substack{\boldsymbol{kpq}\\ q\neq 0}}\frac{4\pi}{q^2}\hat{a}^\dagger_{\boldsymbol{k}+\boldsymbol{q},\sigma}\hat{a}^\dagger_{\boldsymbol{p}-\boldsymbol{q},\sigma'}\hat{a}_{\boldsymbol{p}\sigma'}\hat{a}_{\boldsymbol{k}\sigma} + \\ &\quad \frac{e^2}{2\Omega}\sum_{\sigma\sigma'}\sum_{\boldsymbol{kp}}\frac{4\pi}{\mu^2}\hat{a}^\dagger_{\boldsymbol{k},\sigma}\hat{a}^\dagger_{\boldsymbol{p},\sigma'}\hat{a}_{\boldsymbol{p}\sigma'}\hat{a}_{\boldsymbol{k}\sigma},\end{aligned}$$

where in the last sum we have split the sum over $\boldsymbol{q}$ in two parts, one with $\boldsymbol{q}\neq 0$ and one with $\boldsymbol{q}=0$. In the first term we also let $\mu\rightarrow 0$.

The electron gas, total energy

The last term has the following set of creation and annihilation operatord

$$\hat{a}^{\dagger}_{\boldsymbol{k},\sigma}\hat{a}^{\dagger}_{\boldsymbol{p},\sigma'}\hat{a}_{\boldsymbol{p}\sigma'}\hat{a}_{\boldsymbol{k}\sigma} = -\hat{a}^{\dagger}_{\boldsymbol{k},\sigma}\hat{a}^{\dagger}_{\boldsymbol{p},\sigma'}\hat{a}_{\boldsymbol{k}\sigma}\hat{a}_{\boldsymbol{p}\sigma'} = -\hat{a}^{\dagger}_{\boldsymbol{k},\sigma}\hat{a}_{\boldsymbol{p}\sigma'}\delta_{\boldsymbol{pk}}\delta_{\sigma\sigma'} + \hat{a}^{\dagger}_{\boldsymbol{k},\sigma}\hat{a}_{\boldsymbol{k}\sigma}\hat{a}^{\dagger}_{\boldsymbol{p},\sigma'}\hat{a}_{\boldsymbol{p}\sigma'},$$

which gives

$$\sum_{\sigma\sigma'}\sum_{\boldsymbol{kp}}\hat{a}^{\dagger}_{\boldsymbol{k},\sigma}\hat{a}^{\dagger}_{\boldsymbol{p},\sigma'}\hat{a}_{\boldsymbol{p}\sigma'}\hat{a}_{\boldsymbol{k}\sigma} = \hat{N}^2 - \hat{N},$$

where we have used the expression for the number operator. The term to the first power in $\hat{N}$ goes to zero in the thermodynamic limit since we are interested in the energy per electron E_0/N_e. This term will then be proportional with $1/(\Omega\mu^2)$. In the thermodynamical limit $\Omega \to \infty$ we can set this term equal to zero.

The electron gas, total energy

We then get

$$\hat{H}_{el} = \sum_{\boldsymbol{k}\sigma} \frac{\hbar^2 k^2}{2m} \hat{a}^\dagger_{\boldsymbol{k}\sigma} \hat{a}_{\boldsymbol{k}\sigma} + \frac{e^2}{2\Omega} \sum_{\sigma\sigma'} \sum_{\substack{\boldsymbol{kpq} \\ q\neq 0}} \frac{4\pi}{q^2} \hat{a}^\dagger_{\boldsymbol{k}+\boldsymbol{q},\sigma} \hat{a}^\dagger_{\boldsymbol{p}-\boldsymbol{q},\sigma'} \hat{a}_{\boldsymbol{p}\sigma'} \hat{a}_{\boldsymbol{k}\sigma} + \frac{e^2}{2} \frac{N_e^2}{\Omega} \frac{4\pi}{\mu^2}.$$

The total Hamiltonian is $\hat{H} = \hat{H}_{el} + \hat{H}_b + \hat{H}_{el-b}$. Collecting all our terms we end up with

$$\hat{H}_0 = \sum_{\boldsymbol{k}\sigma} \frac{\hbar^2 k^2}{2m_e} \hat{a}^\dagger_{\boldsymbol{k}\sigma} \hat{a}_{\boldsymbol{k}\sigma},$$

and

$$\hat{H}_I = \frac{e^2}{2\Omega} \sum_{\sigma\sigma'} \sum_{\substack{\boldsymbol{kpq} \\ q\neq 0}} \frac{4\pi}{q^2} \hat{a}^\dagger_{\boldsymbol{k}+\boldsymbol{q},\sigma} \hat{a}^\dagger_{\boldsymbol{p}-\boldsymbol{q},\sigma'} \hat{a}_{\boldsymbol{p}\sigma'} \hat{a}_{\boldsymbol{k}\sigma},$$