

11.4 Hartree-Fock in infinite systems

In the case of homogeneous infinite systems a considerable simplification occurs: from the discussion on the Fermi gas in Sec. 5.1) it is clear that only plane-wave states of definite momentum are appropriate sp states in a translationally invariant system. The determination of the HF orbitals is therefore not needed because the HF basis coincides with the plane-wave basis.

In fact, it is easy to see that also the exact sp propagator⁵,

$$G(\mathbf{p}, \mathbf{p}'; E) = \langle \Psi_0^A | a_{\mathbf{p}} \frac{1}{E - (\hat{H} - E_0^A) + i\eta} a_{\mathbf{p}'}^\dagger | \Psi_0^A \rangle + \langle \Psi_0^A | a_{\mathbf{p}'}^\dagger \frac{1}{E + (\hat{H} - E_0^A) - i\eta} a_{\mathbf{p}} | \Psi_0^A \rangle, \quad (11.157)$$

is automatically diagonal in momentum space, because total momentum $\mathbf{P} = \sum_{i=1}^A \mathbf{p}_i$ is conserved by the Hamiltonian,

$$[\hat{H}, \hat{\mathbf{P}}] = 0, \quad (11.158)$$

and the ground state of the system has definite (zero) total momentum. The propagator in Eq. (11.157) is therefore only nonzero when the same momentum is added and removed from the ground state,

$$G(\mathbf{p}, \mathbf{p}'; E) \equiv \delta_{\mathbf{p}, \mathbf{p}'} G(\mathbf{p}; E). \quad (11.159)$$

We introduce the notation $G(\mathbf{p}; E)$ for the diagonal part of the sp propagator. Also note that because of the isotropy of the system (there is no preferred direction in space) the sp propagator can only depend on the magnitude $p = |\mathbf{p}|$ of the sp momentum \mathbf{p} . As an example, the propagator for a noninteracting system with Hamiltonian

$$\hat{H}_0 = \hat{T} + \hat{U} = \sum_{\mathbf{p}} \frac{\mathbf{p}^2}{2m} a_{\mathbf{p}}^\dagger a_{\mathbf{p}} + \sum_{\mathbf{p}} U(\mathbf{p}) a_{\mathbf{p}}^\dagger a_{\mathbf{p}}, \quad (11.160)$$

becomes,

$$G^{(0)}(\mathbf{p}; E) = \frac{\theta(p - p_F)}{E - \varepsilon(p) + i\eta} + \frac{\theta(p_F - p)}{E - \varepsilon(p) - i\eta}, \quad (11.161)$$

with sp energy $\varepsilon(p) = \mathbf{p}^2/2m + U(p)$. From Eq. (10.2) it follows that also the (irreducible) self-energy is diagonal in momentum space. As a consequence,

⁵For brevity of notation the discussion is restricted to fermions of a single species, but the considerations in Sec. 11.4 hold in general

the Dyson equation becomes an algebraic relationship,

$$G(p; E) = G^{(0)}(p; E) + G(p; E)\Sigma^*(p; E)G(p; E). \quad (11.162)$$

The derivation of the HF approximation for homogeneous infinite systems therefore becomes extremely simple. Since the HF basis necessarily coincides with the plane-wave basis the HF one-body density matrix is, according to Eq. (11.38),

$$n_{\mathbf{p}', \mathbf{p}}^{HF} = \delta_{\mathbf{p}, \mathbf{p}'} \theta(p_F - p), \quad (11.163)$$

equal to the Fermi gas step function.

As a result, the HF self-energy in Eq. (11.13) is given by

$$\Sigma^{HF}(p) = -U(p) + \sum_{\mathbf{p}'} \theta(p_F - p') \langle \mathbf{p}\mathbf{p}' | V | \mathbf{p}\mathbf{p}' \rangle, \quad (11.164)$$

and the HF propagator is

$$G^{HF}(p; E) = \frac{\theta(p - p_F)}{E - \varepsilon^{HF}(p) + i\eta} + \frac{\theta(p_F - p)}{E - \varepsilon^{HF}(p) - i\eta}, \quad (11.165)$$

where

$$\varepsilon^{HF}(p) = \left(\frac{\mathbf{p}^2}{2m} + U(p) \right) + \Sigma^{HF}(p) \quad (11.166)$$

$$= \frac{\mathbf{p}^2}{2m} + \sum_{\mathbf{p}'} \theta(p_F - p') \langle \mathbf{p}\mathbf{p}' | V | \mathbf{p}\mathbf{p}' \rangle, \quad (11.167)$$

is the HF sp energy, independent of the auxiliary potential $U(p)$.

The total energy is, according to Eq. (11.29),

$$\begin{aligned} E^{HF} &= \frac{1}{2} \sum_{\mathbf{p}} \theta(p_F - p) \left[\frac{\mathbf{p}^2}{2m} + \varepsilon^{HF}(p) \right] \\ &= \sum_{\mathbf{p}} \theta(p_F - p) \left[\frac{\mathbf{p}^2}{2m} + \frac{1}{2} \Sigma^{HF}(p) \right] \\ &= T_{FG} + \frac{1}{2} \sum_{\mathbf{p}\mathbf{p}'} \theta(p_F - p) \theta(p_F - p') \langle \mathbf{p}\mathbf{p}' | V | \mathbf{p}\mathbf{p}' \rangle, \end{aligned} \quad (11.168)$$

where $T_{FG} = \frac{3}{5} \frac{p_F^2}{2m}$ is the free Fermi-gas kinetic energy.

Upon inspection, this is the same result as would be obtained in first-order perturbation theory, with the kinetic energy \hat{T} as unperturbed Hamiltonian, and the interaction \hat{V} acting as perturbation term. This is not

surprising, since the translational invariance dictates that the HF ground state and the Fermi-gas ground state coincide,

$$|\Phi_{FG}\rangle = |\Phi_{HF}\rangle = \prod_{p < k_F} a_{\mathbf{p}}^{\dagger} |0\rangle, \quad (11.169)$$

so the first-order correction to the energy of the free Fermi gas is

$$\langle \Phi_{FG} | \hat{V} | \Phi_{FG} \rangle = \frac{1}{2} \sum_{\mathbf{p}\mathbf{p}'} \theta(p_F - p) \theta(p_F - p') \langle \mathbf{p}\mathbf{p}' | V | \mathbf{p}\mathbf{p}' \rangle. \quad (11.170)$$

The HF energy in an infinite system therefore does not go beyond first-order perturbation theory, in contrast to finite systems where the variational determination of the shape of the HF orbitals already includes all orders of perturbation theory.

11.5 Electron gas

We assume for simplicity that we are dealing with the spin-unpolarized electron gas, where equal numbers of spin-up and spin-down electrons are present, or $\rho^{(m_s=+\frac{1}{2})} = \rho^{(m_s=-\frac{1}{2})} = \frac{1}{2}\rho$. The generalization to the spin-polarized case is straightforward (see Exercise 11.7.4). Since the electron-gas Hamiltonian conserves spin, the sp propagator and self-energy are diagonal in the spin projection quantum number m_s .

According to Eq. (11.164) the HF self-energy for the electron gas is

$$\Sigma^{HF}(\mathbf{p}_1 m_{s_1}) = \sum_{\mathbf{p}_2 m_{s_2}} \theta(p_F - p_2) \langle \mathbf{p}_1 m_{s_1}, \mathbf{p}_2 m_{s_2} | V' | \mathbf{p}_1 m_{s_1}, \mathbf{p}_2 m_{s_2} \rangle, \quad (11.171)$$

with Fermi momentum $p_F = [3\pi^2 \rho]^{\frac{1}{3}}$.

The antisymmetrized matrix element in Eq. (11.171) is given by

$$\begin{aligned} \langle \mathbf{p}_1 m_{s_1}, \mathbf{p}_2 m_{s_2} | V' | \mathbf{p}_1 m_{s_1}, \mathbf{p}_2 m_{s_2} \rangle &= (\mathbf{p}_1 m_{s_1}, \mathbf{p}_2 m_{s_2} | V' | \mathbf{p}_1 m_{s_1}, \mathbf{p}_2 m_{s_2}) \\ &\quad - (\mathbf{p}_1 m_{s_1}, \mathbf{p}_2 m_{s_2} | V' | \mathbf{p}_2 m_{s_2}, \mathbf{p}_1 m_{s_1}) \\ &= -\delta_{m_{s_1}, m_{s_2}} \frac{4\pi}{V} \frac{1}{|\mathbf{p}_1 - \mathbf{p}_2|^2}. \end{aligned} \quad (11.172)$$

The first (direct or Hartree) term in Eq. (11.172) is zero according to the definition (5.32) for V' (no relative momentum is transferred). Only the

second (exchange or Fock) term remains and the HF self-energy becomes

$$\Sigma^{HF}(p_1) = - \sum_{\mathbf{p}_2} \theta(p_F - p_2) \frac{4\pi}{V} \frac{1}{|\mathbf{p}_1 - \mathbf{p}_2|^2}, \quad (11.173)$$

which (as was also clear from symmetry arguments) is independent of m_s .

Taking the thermodynamic limit and replacing the discrete sums over momentum with integrations leads to,

$$\begin{aligned} \Sigma^{HF}(p_1) &= - \frac{V}{(2\pi)^3} \frac{4\pi}{V} \int d\mathbf{p}_2 \theta(p_F - p_2) \frac{1}{|\mathbf{p}_1 - \mathbf{p}_2|^2} \\ &= - \frac{1}{\pi} \int_0^{p_F} dp_2 p_2^2 \int_{-1}^{+1} dx \frac{1}{p_1^2 + p_2^2 - 2xp_2p_1} \\ &= - \frac{k_F}{\pi u_1} \int_0^1 du_2 u_2 \ln \left| \frac{u_2 + u_1}{u_2 - u_1} \right|, \end{aligned} \quad (11.174)$$

where the angular integration has been performed and dimensionless variables $u_2 = p_2/p_F$ and $u_1 = p_1/p_F$ were introduced. The remaining integral in Eq. (11.174) can be calculated using the standard primitives

$$x^n \ln|x| = \frac{d}{dx} \left[\frac{x^{n+1}}{n+1} \left(\ln|x| - \frac{1}{n+1} \right) \right], \quad (11.175)$$

and after some algebra, the HF exchange potential becomes

$$\Sigma^{HF}(p) = - \frac{p_F}{\pi} \left(1 + \frac{1-u^2}{2u} \ln \left| \frac{1+u}{1-u} \right| \right). \quad (11.176)$$

Special values are $\Sigma^{HF}(0) = -2\frac{p_F}{\pi}$ and $\Sigma^{HF}(p_F) = -\frac{p_F}{\pi}$. The HF sp energies $\varepsilon^{HF}(p)$ are obtained by adding the kinetic energy contribution,

$$\varepsilon^{HF}(p) = \frac{p^2}{2} + \Sigma^{HF}(p). \quad (11.177)$$

The HF potential $\Sigma^{HF}(p)$ and sp energy $\varepsilon^{HF}(p)$ are plotted in Fig. 11.6 as a function of $u = p/p_F$. The HF potential is negative, monotonously increasing, and goes to zero like

$$\Sigma^{HF}(p) \rightarrow - \frac{2}{3} \frac{p_F}{\pi} \frac{1}{u^2}, \quad (11.178)$$

in the $p \rightarrow \infty$ limit. Its main effect is a lowering of the sp energies $\varepsilon^{HF}(p)$ compared to the free sp spectrum.

The HF ground-state energy is, according to Eq. (11.29),

$$E^{HF} = \frac{1}{2} \sum_{\mathbf{p}m_s} \theta(p_F - p) \left[\frac{p^2}{2} + \varepsilon^{HF}(p) \right] = T_{FG} + E_x, \quad (11.179)$$

and consists of the Fermi-gas kinetic energy T_{FG}

$$T_{FG} = N \frac{3}{10} p_F^2, \quad (11.180)$$

to which the (negative) exchange energy E_x has been added,

$$E_x = \frac{1}{2} \sum_{\mathbf{p}m_s} \theta(p_F - p) \Sigma^{HF}(p) = N \left(-\frac{3}{4\pi} p_F \right). \quad (11.181)$$

Obtaining the last equality again requires the use of the primitives (11.175).

In Fig. 11.7 the density dependence of the HF energy for the spin-unpolarized electron gas,

$$E^{HF}/N = \frac{3}{10} p_F^2 - \frac{3}{4\pi} p_F \quad (11.182)$$

is displayed. Following convention, we do this as a function of

$$r_s = \left[\frac{3}{4\pi\rho} \right]^{\frac{1}{3}} = \left[\frac{4}{9\pi} \right]^{\frac{1}{3}} \frac{1}{k_F} \quad (11.183)$$

being the radius (in atomic units) of a sphere containing one electron. Note that because of the variational nature of HF, the exact energy lies below this curve, so the electron gas is definitely bound for densities lower than $r_s \approx 2.5$. This may seem surprising in view of the repulsive Coulomb force between the electrons; this repulsion is globally compensated, however, by the attractive interaction with the positive background. The residual effect is dominated by the attractive exchange potential, and this provides an explanation for the cohesion energy of metals, where the valence electrons move in the (lattice) background of the positive ions. As a matter of fact, the equilibrium point in the HF description of the electron gas (corresponding to the minimum at $r_s = 4.82$ and $E/N = -0.0475$ in the energy versus density curve in Fig. 11.7) roughly agrees with the experimental situation in solid Na ($r_s = 3.96$ and cohesion energy $E/N = -0.0415$).

The HF energy becomes exact in the limit of large densities, as can be seen on the basis of simple scaling arguments: taking the Fermi momentum as the natural scale, the electron gas Hamiltonian in Eq. (5.31) can be

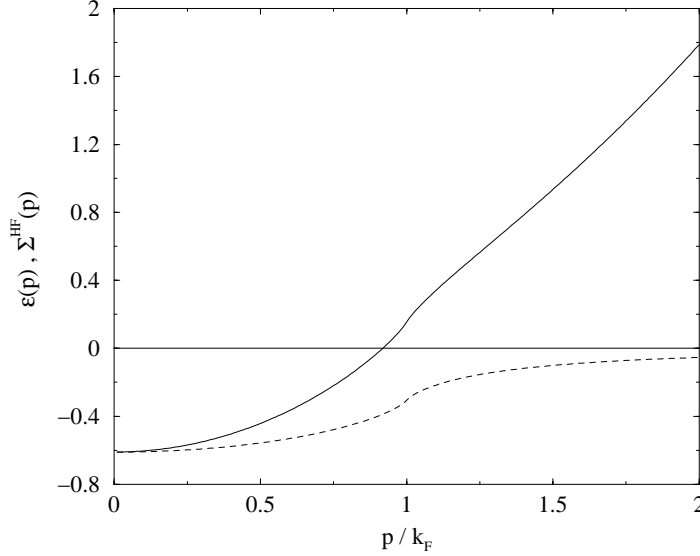


Fig. 11.6 HF potential (dashed line) and corresponding sp energy in the electron gas.

rewritten as

$$\hat{T} = p_F^2 \left[\sum_{\mathbf{p}m_s} \frac{(p/p_F)^2}{2} a_{\mathbf{p}m_s}^\dagger a_{\mathbf{p}m_s} \right] \quad (11.184)$$

$$\hat{V}' = p_F \left[\frac{1}{2} \sum_{\substack{\mathbf{P}, \mathbf{p} \neq \mathbf{p}' \\ m_{s_1} m_{s_2}}} \frac{4\pi}{(V p_F^3)} \frac{1}{[(\mathbf{p}/p_F) - (\mathbf{p}'/p_F)]^2} \right. \\ \left. \times a_{\frac{1}{2}\mathbf{P}+\mathbf{p}, m_{s_1}}^\dagger a_{\frac{1}{2}\mathbf{P}-\mathbf{p}, m_{s_2}}^\dagger a_{\frac{1}{2}\mathbf{P}-\mathbf{p}', m_{s_1}} a_{\frac{1}{2}\mathbf{P}+\mathbf{p}', m_{s_2}} \right],$$

where the operators inside the brackets contain only dimensionless quantities. As a consequence, in the limit of large density ($k_F \rightarrow \infty$) the kinetic term dominates and the system approaches a free Fermi gas. The Coulomb interaction acts as a small perturbation, and first-order perturbation theory leads precisely to the HF result (see Sec. 11.4). One can show that all higher-order terms in a perturbation expansion in powers of \hat{V} are divergent, and that an infinite set of higher-order terms must be summed in order to get a finite result. In a large-density expansion of the electron-gas energy the dominant term beyond HF is in fact logarithmic, a result that

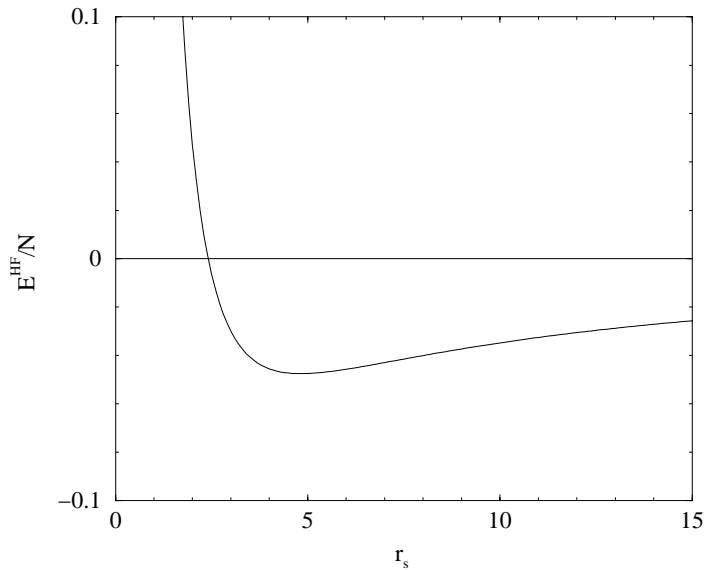


Fig. 11.7 Binding energy per particle for the electron gas, in the HF approximation.

will be derived in Sec. 14.5.

11.6 Nuclear matter

The HF approximation leads to miserable results for nuclear matter, when realistic nucleon-nucleon (NN) potentials with strong short-range repulsion are used. It is nevertheless instructive to derive the HF expressions, as it is an ingredient in more elaborate theories (and provides a good exercise in handling isospin and spin degrees of freedom).

We consider symmetric (equal numbers of protons and neutrons) and spin-unpolarized nuclear matter, which is a Fermi gas with degeneracy equal to four. The expression for the HF self-energy is

$$\Sigma^{HF}(p_1) = \sum_{\mathbf{p}_2 m_{s_2} m_{t_2}} \theta(p_F - p_2) \langle \mathbf{p}_1 m_{s_1} m_{t_1}, \mathbf{p}_2 m_{s_2} m_{t_2} | V | \mathbf{p}_1 m_{s_1} m_{t_1}, \mathbf{p}_2 m_{s_2} m_{t_2} \rangle. \quad (11.185)$$

The NN interaction is usually known in the form of a partial-wave decomposition. Introducing center-of-mass momentum \mathbf{P} and relative mo-

mentum \mathbf{p} , we have

$$\langle \mathbf{P}p(LS)JT | V | \mathbf{P}'p'(L'S')J'T' \rangle = \delta_{\mathbf{P},\mathbf{P}'} \delta_{J,J'} \delta_{T,T'} \delta_{S,S'} \frac{4\pi}{V} V_{LL'}^{STJ}(p, p'), \quad (11.186)$$

which are the matrix elements in the two-nucleon basis defined in Eq. (8.10), including the coupling to total spin S and isospin T , and where the orbital relative angular momentum L couples with S to total internal angular momentum J .

With the aid of the basis transformation in Eq. (8.10) one can express the HF sp potential as

$$\begin{aligned} \Sigma^{HF}(p_1) &= \frac{1}{16\pi^3} \int d\mathbf{p}_2 \theta(p_F - p_2) \sum'_{LST} (2T+1)(2J+1) \\ &\quad V_{LL}^{STJ}(|\mathbf{p}_1 - \mathbf{p}_2|, |\mathbf{p}_1 - \mathbf{p}_2|), \end{aligned} \quad (11.187)$$

where the primed summation is restricted to odd values of $L + S + T$.

The HF ground-state energy for nuclear matter can be evaluated using Eq. (11.187), and typically does not even predict binding for nuclear matter. For the CDBonn potential, e.g., one finds an energy per nucleon of 4.64 MeV, and for the old Reid Soft Core potential (which has a much stronger repulsive core) even 176.25 MeV.

The underlying reason is the Slater-determinant nature of the HF ground state, which allows two nucleons to come close together and experience the strong short-range repulsion of the NN potential. A more reasonable description requires the inclusion of additional short-range correlations between the nucleons, which is the subject of Sec. 15.2.

11.7 Exercises

(1) Prove Brillouin's theorem in Eq. (11.60) by direct calculation of the matrix element $\langle \Phi_{HF}^A | \hat{H} a_p^\dagger a_h | \Phi_{HF}^A \rangle$, with $|\Phi_{HF}^A\rangle = \prod_h a_h^\dagger |0\rangle$ and

$$\hat{H} = \sum_{\alpha\gamma} \langle \alpha | T | \gamma \rangle a_\alpha^\dagger a_\gamma + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta | V | \gamma\delta \rangle a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma. \quad (11.188)$$

(2) Prove Koopman's theorem in Eq. (11.61) by direct calculation of the matrix element $\langle \Phi_{HF}^A | a_h^\dagger \hat{H} a_h | \Phi_{HF}^A \rangle$.

(3) Generate the dissociation curve in Fig. 11.4 for the H_2 molecule using the two-dimensional model in Sec. 11.3.3.

(4) For the spin-polarized electron gas one can define the asymmetry parameter ξ as

$$\xi = \frac{\rho^{(+\frac{1}{2})} - \rho^{(-\frac{1}{2})}}{\rho}, \quad (11.189)$$

where $\rho^{(m_s)}$ is the density of the spin-up or spin-down electrons and $\rho = \sum_{m_s} \rho^{(m_s)}$ is the total electron density. Show that:

(a) The Fermi momenta of the spin-up and spin-down electrons are

$$p_F^{(m_s)} = [6\pi^2 \rho^{(m_s)}]^{1/3} = (1 \pm \xi)p_F, \quad (11.190)$$

where $p_F = [3\pi^2 \rho]^{1/3}$ is the Fermi momentum of the unpolarized electron gas at the same density.

(b) The Fermi-gas kinetic energy is

$$T_{FG}(\xi) = T_{FG}(0) \frac{1}{2} [(1 + \xi)^{5/3} + (1 - \xi)^{5/3}], \quad (11.191)$$

where $T_{FG}(0)$ is the kinetic energy in Eq. (11.180) for the unpolarized electron gas at the same density.

(c) The HF self-energy is

$$\begin{aligned} \Sigma^{HF(m_s)}(\xi; p) = & \quad (11.192) \\ & -\frac{p_F}{\pi} \left((1 \pm \xi)^{1/3} + \frac{(1 \pm \xi)^{2/3} - u^2}{2u} \ln \left| \frac{(1 \pm \xi)^{1/3} + u}{(1 \pm \xi)^{1/3} - u} \right| \right), \end{aligned}$$

where $u = p/p_F$.

(d) The HF exchange energy is

$$E_x(\xi) = E_x(0) \frac{1}{2} [(1 + \xi)^{4/3} + (1 - \xi)^{4/3}], \quad (11.193)$$

where $E_x(0)$ is the exchange energy in Eq. (11.181) for the unpolarized electron gas at the same density.

(5) Derive the expression in Eq. (11.187) for the HF potential in nuclear matter.

