Chapter 11

Mean-field or Hartree-Fock approximation at $T = 0$

In the previous chapter the formulation of many-body theory in terms of self-consistent Green functions was developed. The present chapter deals with the implementation of the theory in lowest order, which is equivalent to the so-called mean-field or Hartree-Fock (HF) approximation. The formal equations of the HF method are derived in Sec. 11.1 together with detailed considerations of the resulting HF propagator. These results are then immediately contrasted with the conventional derivation of the HF method by means of the variational principle. Section 11.1 also contains a formulation of the HF equations in coordinate space together with a discussion of restricted and unrestricted implementations of the method. In Sec. 11.2 the application of this method to atoms is presented. This section includes a discussion of closed-shell atoms, a comparison with experimental data, and some consideration of numerical details necessary for a successful implementation of the method. Suggested steps to develop a numerical procedure for solving the relevant equations are also presented. The application of the HF method to molecules is presented in Sec. 11.3. This includes a brief discussion of the Born-Oppenheimer method, the use of finite, discrete basis sets, and a discussion of the hydrogen molecule. The relevant considerations for the application of the HF method to infinite systems are presented in Sec. 11.4. Application of this method to the electron gas (11.5) and nuclear matter (11.6) complete this chapter on the HF method for fermions.

11.1 The Hartree-Fock formalism

11.1.1 *Derivation of the Hartree-Fock equations*

The Hartree-Fock equations will be derived here in the general context established in Sec. 3.1, for a Hamiltonian

$$\hat{H} = \hat{T} + \hat{V} = \left(\hat{T} + \hat{U}\right) + \left(\hat{V} - \hat{U}\right), \tag{11.1}$$

which includes an appropriately chosen (but in principle arbitrary) auxiliary potential $\hat{U}$. The sp basis that we use is the one where the noninteracting Hamiltonian

$$\hat{H}_0 = \hat{T} + \hat{U} = \sum_{\alpha} \varepsilon_\alpha a_\alpha^\dagger a_\alpha \tag{11.2}$$

is diagonal. The unperturbed sp propagator $G^{(0)}$ therefore corresponds to

$$G^{(0)}(\alpha, \beta; E) = \delta_{\alpha,\beta} \left[\frac{\theta(\alpha - F)}{E - \varepsilon_\alpha + i\eta} + \frac{\theta(F - \alpha)}{E - \varepsilon_\alpha - i\eta} \right]. \tag{11.3}$$

We start with the general expression in Eq. (10.31) for the (irreducible) self-energy Σ^* in terms of the 4-point vertex function Γ. The simplest thing to do at this stage is to set[1] $\Gamma = 0$. Clearly, this implies that for the system under study the tp propagator is dominated by the noninteracting contribution in Eq. (10.22). Having made the present choice of self-energy, it will be shown shortly that it leads to a mean-field description. It was anticipated in Ch. 3 that this would be a reasonable approximation for atoms. The quality of this approximation can be tested by comparing the corresponding results with the relevant experimental data. This comparison should include those data accessible with the sp propagator but can also involve two-particle properties in order to assess the validity of the approximation to Eq. (10.22) implied by setting $\Gamma = 0$. This approximation leads to the so-called Hartree-Fock approximation, and the resulting self-energy reads [see Eq. (10.31)],

$$\Sigma^{HF}(\gamma, \delta; E) = -\langle \gamma | U | \delta \rangle - i \int_{C\uparrow} \frac{dE'}{2\pi} \sum_{\mu\nu} \langle \gamma\mu | V | \delta\nu \rangle G^{HF}(\nu, \mu; E'). \tag{11.4}$$

[1]Note that this corresponds, according to Eq. (10.22), to replacing the tp propagator G_{II} with the antisymmetrized product of two sp propagators, an approximation which would be exact for a non-interacting system.

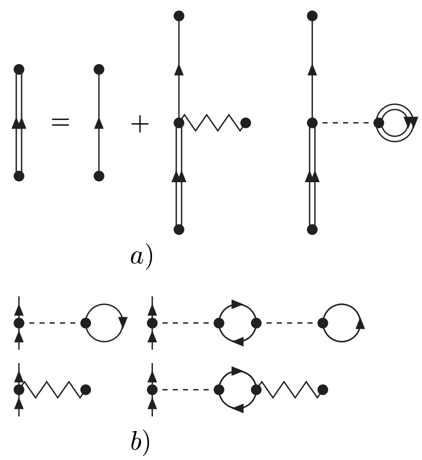

Fig. 11.1 Part *a*) shows the diagrammatic representation of the Dyson equation in the Hartree-Fock approximation. In part *b*) all diagrams up to second order contributing to the HF (irreducible) self-energy are displayed.

In keeping with the self-consistent formulation of Sec. 10.4, the HF propagator G^{HF} appearing in Eq. (11.4) is *not* the noninteracting propagator $G^{(0)}$, but rather the solution of the corresponding Dyson equation,

$$G^{HF}(\alpha,\beta;E) = G^{(0)}(\alpha,\beta;E) + \sum_{\gamma\delta} G^{(0)}(\alpha,\gamma;E)\Sigma^{HF}(\gamma,\delta)G^{HF}(\delta,\beta;E), \tag{11.5}$$

where the energy dependence of the HF self-energy has been eliminated. This is appropriate as can be inferred from inspection of Eq. (11.4) and will be shown in more detail below. The diagrammatic equivalent of Eq. (11.5) is shown in Fig. 11.1*a*). It is clear that a particular, infinite class of self-energy diagrams is retained in the HF self-energy, of which the lowest-order ones are shown in Fig. 11.1*b*). We emphasize that the symmetrized version of the diagram method is employed so that both a direct and an exchange contribution are implied for each interaction V.

Further analysis of the HF self-energy Σ^{HF} in Eq. (11.4) requires the energy-dependence of the (as yet unknown) HF propagator, but we may assume that it has the same simple pole structure as the exact propagator and write its Lehmann representation (see Sec. 8.2) as

$$G^{HF}(\alpha,\beta;E) = \sum_m \frac{z_\alpha^{m+} z_\beta^{m+^*}}{E - \varepsilon_m^+ + i\eta} + \sum_n \frac{z_\alpha^{n-} z_\beta^{n-^*}}{E - \varepsilon_n^- + i\eta}, \tag{11.6}$$

where the (approximate) z amplitudes are defined in analogy to Eq. (10.36) by

$$z_\alpha^{n-} = \left\langle \Psi_n^{A-1} \right| a_\alpha \left| \Psi_0^A \right\rangle . \tag{11.7}$$

and

$$z_\alpha^{n+} = \left\langle \Psi_0^{A} \right| a_\alpha \left| \Psi_n^{A+1} \right\rangle , \tag{11.8}$$

respectively. The energies $\varepsilon^\pm$ are defined in accord with Eq. (10.34) and given by

$$\varepsilon_n^- = E_0^A - E_n^{A-1} \tag{11.9}$$

and

$$\varepsilon_n^+ = E_n^{A+1} - E_0^A . \tag{11.10}$$

The assumption implied by the form of Eq. (11.6) will be correct if it is subsequently found that the Dyson equation is indeed solved by this form of the HF propagator.

Using Eq. (11.6) the HF self-energy can be readily evaluated,

$$\Sigma^{HF}(\gamma,\delta) = -\langle\gamma|\,U\,|\delta\rangle + \sum_{\mu\nu} \langle\gamma\mu|\,V\,|\delta\nu\rangle \sum_n z_\nu^{n-^*} z_\mu^{n-}, \tag{11.11}$$

where the energy argument of Σ^{HF} was appropriately dropped since the HF self-energy is clearly independent of the energy E. Recalling the relationships of Sec. 8.4 between the one-body density matrix of the system and the removal amplitudes in the sp propagator [see Eq. (8.20)], the HF one-body density matrix $n_{\mu\nu}^{HF}$ may be defined as

$$n_{\mu\nu}^{HF} = \sum_n z_\nu^{n-} z_\mu^{n-^*}, \tag{11.12}$$

and the HF self-energy is written in a transparant form as

$$\Sigma^{HF}(\gamma,\delta) = -\langle\gamma|\,U\,|\delta\rangle + \sum_{\mu\nu} \langle\gamma\mu|\,V\,|\delta\nu\rangle\, n_{\mu\nu}^{HF} . \tag{11.13}$$

This expression shows that the HF self-energy really represents a “mean field” or average potential, in the sense that it contains the interparticle interaction V, averaged over the one-body density matrix. The latter quantity takes into account the occupancies of the different sp orbitals in the ground state.

The fact that Σ^{HF} is just a static (energy-independent) sp potential also implies that the Dyson equation Eq. (11.5) is equivalent to an independent particle problem. The bound sp eigenstates of $H_0 + \Sigma^{HF}$ can therefore be obtained by transforming the Dyson equation to an eigenvalue equation, using the standard limit procedure of Secs. 7.3 and 10.5. The limit

$$\lim_{E \to \varepsilon_n^-} (E - \varepsilon_n^-) \left\{ G^{HF} = G^{(0)} + G^{(0)} \; \Sigma^{HF} \; G^{HF} \right\}, \tag{11.14}$$

leads to the Hartree-Fock eigenvalue equations

$$\sum_{\delta} \left\{ \varepsilon_\delta \delta_{\alpha,\delta} - \langle \alpha | \, U \, | \delta \rangle + \sum_{\mu\nu} \langle \alpha\mu | \, V \, | \delta\nu \rangle \, n_{\mu\nu}^{HF} \right\} z_\delta^{n-} = \varepsilon_n^- z_\alpha^{n-}. \tag{11.15}$$

The HF equations determine the unknown removal energies ε_n^- and amplitudes z_α^{n-}. The latter should be normalized to unity,

$$\sum_{\alpha} |z_\alpha^{n-}|^2 = 1, \tag{11.16}$$

because of the energy-independence of the HF self-energy, as was discussed in Sec. 7.3. The particle-number sum rule

$$\sum_{n\alpha} |z_\alpha^{n-}|^2 = \sum_{\alpha} n_{\alpha\alpha}^{HF} = A \tag{11.17}$$

then dictates that there are exactly A removal states in the Lehmann representation of Eq. (11.6), which should be identified with the A lowest-energy solutions z_α^{n-} $(n = 1, \ldots, A)$ of the HF equations. This is of course just what we expect for the propagator of an independent-particle system as discussed in Sec. 8.5.

While the HF eigenvalue equations in Eq. (11.15) may *look* like a sp Schrödinger equation corresponding to a noninteracting many-body system, there is one complication: due to the self-consistency condition Eq. (11.12) the equations are actually non-linear in the amplitudes z_α^{n-}. The HF equations are therefore usually solved by iteration: starting from the A lowest-energy sp orbitals $\alpha = 1, \ldots, A$ of H_0 one sets

$$\text{(Initial guess)} \;\; \rightarrow \quad z_\alpha^{n-} = \delta_{n,\alpha}, \tag{11.18}$$

and uses this first approximation to construct the corresponding self-energy Σ^{HF} through Eq. (11.11). Then the A lowest-energy solutions of the Hamiltonian $H_0 + \Sigma^{HF}$ are determined (which is equivalent to solving a noninteracting system), yielding new z_α^{n-}. This cycle is repeated until convergence is achieved and the amplitudes z_α^{n-} no longer change during successive iterations. A more detailed look at practical methods for solving the HF equations in the case of atoms can be found in Sec. 11.2.

Finally we note that the derivation up to now has used the sp basis that diagonalizes the Hamiltonian $H_0 = T + U$, i.e.

$$\langle\alpha| T |\delta\rangle + \langle\alpha| U |\delta\rangle = \varepsilon_\delta \; \delta_{\alpha,\delta}. \tag{11.19}$$

Substituting this result into Eq. (11.15) we see that the matrix elements of the auxiliary potential U cancel, and the HF equations become

$$\sum_\delta \left\{ \langle\alpha| T |\delta\rangle + \sum_{\mu\nu} \langle\alpha\mu| V |\delta\nu\rangle \, n_{\mu\nu}^{HF} \right\} z_\delta^{n-} = \varepsilon_n^- z_\alpha^{n-}. \tag{11.20}$$

The HF equations are therefore independent of the auxiliary field U - as it should be in the framework of self-consistent Green function theory - and Eq. (11.20) therefore represents the HF equations in an arbitrary sp basis. Of course, a suitable choice of the auxiliary field may speed up convergence of the iterative solution. In the nuclear case, e.g., one can start with an auxiliary potential which provides localization of the nucleons, as was discussed in Sec. 3.1.

11.1.2 *The Hartree-Fock propagator*

The HF self-consistency problem consists of the determination of the removal amplitudes z_α^{n-} and energies ε_n^- $(n = 1, \ldots, A)$ which solve Eqs. (11.12) and (11.20). After this is achieved we can construct the remaining eigenstates $(n = A+1, A+2, \ldots)$ in Eq. (11.20) having higher sp energies. These correspond to the particle addition amplitudes z_β^{m+} and energies ε_m^+ in Eq. (11.6), so we write

$$\sum_\delta \left\{ \langle\alpha| T |\delta\rangle + \sum_{\mu\nu} \langle\alpha\mu| V |\delta\nu\rangle \, n_{\mu\nu}^{HF} \right\} z_\delta^{m+} = \varepsilon_m^+ z_\alpha^{m+}. \tag{11.21}$$

Note that Eq. (11.21) is an ordinary eigenvalue problem since the one-body density matrix,

$$n_{\mu\nu}^{HF} = \sum_{n=1}^{A} z_\nu^{n-} z_\mu^{n-^*}, \tag{11.22}$$

is determined by the removal amplitudes and therefore fixed. No additional self-consistency steps are thus required.

The construction of the HF propagator of Eq. (11.6) is now complete, and all physical observables contained in the sp propagator (see Sec. 8.3-8.4) can be evaluated in the HF approximation. We have, e.g., that the excited states $\left|\Psi_n^{A-1}\right\rangle$ in the $A-1$ particle system which can be reached by the removal of one particle from the A particle ground state $\left|\Psi_0^A\right\rangle$ have a spectrum

$$\text{(HF:)} \qquad E_0^A - E_n^{A-1} = \varepsilon_n^-, \tag{11.23}$$

and removal amplitudes

$$\text{(HF:)} \qquad \left\langle \Psi_n^{A-1}\right| a_\alpha \left|\Psi_0^A\right\rangle = z_\alpha^{n-}. \tag{11.24}$$

The interpretation of the HF sp energies ε_n^- as removal energies follows naturally from the propagator formulation. It is less obvious in a variational context (see Sec. 11.1.3), where it is called Koopman's theorem. For the excited states of the $A+1$ particle system we have likewise for the spectrum

$$\text{(HF:)} \qquad E_n^{A+1} - E_0^A = \varepsilon_n^+, \tag{11.25}$$

and the addition amplitudes

$$\text{(HF:)} \qquad \left\langle \Psi_0^{A}\right| a_\alpha \left|\Psi_n^{A+1}\right\rangle = z_\alpha^{n+}. \tag{11.26}$$

The hole part of the spectral function defined in Eq. (8.11) reads

$$\text{(HF:)} \qquad S_h(\alpha, E) = \sum_{n=1}^{A} |z_\alpha^{n-}|^2 \delta(E - \varepsilon_n^-), \tag{11.27}$$

and the corresponding mean removal energy is

$$\text{(HF:)} \qquad \overline{R}_{HF} = \sum_\alpha \int_{-\infty}^{\varepsilon_F^-} dE \; E \; S_h(\alpha, E) = \sum_{n=1}^{A} \varepsilon_n^-. \tag{11.28}$$

The HF result for the ground-state energy then follows from Eq. (8.26),

$$\begin{aligned} \text{(HF:)} \qquad E_0^A &= \frac{1}{2}\left\{ \sum_{\alpha\beta} \langle\alpha|\, T \,|\beta\rangle \; n_{\alpha\beta}^{HF} + \sum_{n=1}^{A} \varepsilon_n^- \right\}, \\ &= \frac{1}{2}\left\{ \overline{T}_{HF} + \overline{R}_{HF} \right\}. \end{aligned} \tag{11.29}$$

Obviously, $\overline{T}_{HF}$ represents the expectation value of the one-body part of the Hamiltonian (the kinetic energy and, if present, the external potential), since according to Eq. (8.19) we have

$$\text{(HF:)} \qquad \left\langle \Psi_0^A \right| \hat{T} \left| \Psi_0^A \right\rangle = \sum_{\alpha\beta} \langle \alpha | \, T \, | \beta \rangle \;\, n_{\alpha\beta}^{HF} = \overline{T}_{HF}. \tag{11.30}$$

The contribution of the two-body interaction $\hat{V}$ to the ground-state energy can now be expressed in terms of the HF quantities $\overline{R}_{HF}$ and $\overline{T}_{HF}$,

$$\text{(HF:)} \qquad \left\langle \Psi_0^A \right| \hat{V} \left| \Psi_0^A \right\rangle = \overline{V}_{HF} = E_0^A - \overline{T}_{HF}$$
$$= \frac{1}{2}(\overline{R}_{HF} - \overline{T}_{HF}). \tag{11.31}$$

An alternative expression for $\overline{R}_{HF} = \sum_{n=1}^{A} \epsilon_n^-$ is obtained by multiplying Eq. (11.20) with z_α^{n-*}, followed by a summation over α and over $n = 1, \ldots, A$. The resulting expression,

$$\sum_{n=1}^{A} \varepsilon_n^- = \sum_{\alpha\delta} \left\{ \langle \alpha | \, T \, | \delta \rangle + \sum_{\mu\nu} \langle \alpha\mu | \, V \, | \delta\nu \rangle \;\, n_{\mu\nu}^{HF} \right\} n_{\alpha\delta}^{HF} \tag{11.32}$$

$$= \overline{T}_{HF} + \sum_{\alpha\beta\mu\nu} \langle \alpha\mu | \, V \, | \beta\nu \rangle \, n_{\mu\nu}^{HF} n_{\alpha\beta}^{HF}, \tag{11.33}$$

when substituted in Eq. (11.31), implies that

$$\overline{V}_{HF} = \frac{1}{2} \sum_{\alpha\beta\mu\nu} \langle \alpha\mu | \, V \, | \beta\nu \rangle \;\, n_{\mu\nu}^{HF} n_{\alpha\beta}^{HF}. \tag{11.34}$$

As a consequence, the HF ground-state energy can also be expressed as

$$\text{(HF:)} \qquad E_0^A = \overline{R}_{HF} - \overline{V}_{HF} \tag{11.35}$$

$$= \sum_{n=1}^{A} \varepsilon_n^- - \frac{1}{2} \sum_{\alpha\beta\mu\nu} \langle \alpha\mu | \, V \, | \beta\nu \rangle \;\, n_{\mu\nu}^{HF} n_{\alpha\beta}^{HF}. \tag{11.36}$$

Clearly, E_0^A is *not* just the sum of the HF sp energies of the occupied orbitals, as it would be for an independent-particle problem. The correction term $-\overline{V}_{HF}$ in Eq. (11.36) is sometimes called the rearrangement energy.

Up to now the HF propagator $G^{HF}(\alpha, \beta; E)$ and all related quantities have been expressed in an arbitrary sp basis. However, once the removal amplitudes z_α^{n-} have been fixed, Eqs. (11.20) and 11.21) constitute an (hermitian) eigenvalue problem. The solutions $z_\alpha^{n\pm}$ therefore define an orthonormal basis set of HF sp states,

$$\left| n^\pm \right\rangle = \sum_\alpha z_\alpha^{n\pm} \left| \alpha \right\rangle. \tag{11.37}$$

For clarity we will continue to label the HF sp states with roman letters, but we drop the ($\pm$) superscripts: from the propagator context it is obvious that the HF sp states corresponding to the A lowest sp energies (the *hole* states) should be interpreted as corresponding to removal amplitudes, whereas the HF sp states with higher-lying energies (the *particle* states) correspond to addition amplitudes.

Expressed in the HF basis, the HF one-body density matrix is simply (using the step function for the case when its argument is true or false)

$$n_{ij}^{HF} = \delta_{i,j}\ \theta(1 \leq i \leq A), \tag{11.38}$$

and the defining equation [see Eqs. (11.20) and (11.21)] for the HF basis becomes

$$\langle n|\, T\, |m\rangle + \sum_{i=1}^{A} \langle ni|\, V\, |mi\rangle = \delta_{m,n}\varepsilon_n. \tag{11.39}$$

The HF propagator is also diagonal in the HF basis,

$$G^{HF}(m,n;E) = \delta_{m,n}\left[\frac{\theta(n>A)}{E-\varepsilon_n+i\eta} + \frac{\theta(1\leq n\leq A)}{E-\varepsilon_n-i\eta}\right]. \tag{11.40}$$

Eq. (11.40) is recognized as the propagator of a noninteracting system with sp hamiltonian

$$\hat{H}_{HF} = \sum_n \varepsilon_n a_n^\dagger a_n, \tag{11.41}$$

$$= \sum_{mn} \langle n|\, T\, |m\rangle\, a_n^\dagger a_m + \sum_{nm}\left(\sum_{i=1}^{A} \langle ni|\, V\, |mi\rangle\right) a_n^\dagger a_m, \tag{11.42}$$

and this would seem to imply that the HF ground state can be identified with the Slater determinant

$$\text{(HF:)} \qquad \left|\Psi_0^A\right\rangle \to \left|\Phi_{HF}^A\right\rangle = \prod_{i=1}^{A} a_i^\dagger \left|0\right\rangle. \tag{11.43}$$

It is readily checked that Eqs. (11.30) and (11.34) are indeed consistent with the HF ground state in Eq. (11.43), i.e.

$$\begin{aligned} \overline{T}_{HF} &= \left\langle \Phi_{HF}^A\right|\hat{T}\left|\Phi_{HF}^A\right\rangle \\ \overline{V}_{HF} &= \left\langle \Phi_{HF}^A\right|\hat{V}\left|\Phi_{HF}^A\right\rangle. \end{aligned} \tag{11.44}$$

That this interpretation is correct is also borne out by the variational derivation in the next section.

11.1.3 *Variational content of the HF approximation*

The eigenstates for a system of A non-interacting fermions have been discussed in Section 3.1. They have the simple form of antisymmetrized product states and may generically be written as

$$\left|\Phi^A\right\rangle = \prod_{i=1}^{A} a^\dagger_{h_i} \left|0\right\rangle , \tag{11.45}$$

in terms of A orthonormal occcupied sp orbitals $a^\dagger_{h_i}$. The orthonormality condition ensures a proper normalization, $\left\langle \Phi^A \middle| \Phi^A \right\rangle = 1$.

The product states in Eq. (11.45), also called independent particle states or Slater determinants, of course far from exhaust the complete A-particle Fock space, but since the occupied sp orbitals can be chosen at will, there is considerable freedom left in the set of all $\left|\Phi^A\right\rangle$. If we now consider an interacting system with Hamiltonian $\hat{H} = \hat{T} + \hat{V}$, we may approximate the exact interacting ground state by determining the independent particle state $\left|\Phi^A\right\rangle$ which minimizes the expectation value $\left\langle \Phi^A \right| \hat{H} \left|\Phi^A\right\rangle$ of the Hamiltonian. In the case of weak interparticle interactions $\hat{V}$ this is usually a good starting point.

The expectation value is easily evaluated as

$$E = \left\langle \Phi^A \right| \hat{H} \left|\Phi^A\right\rangle = \sum_{i=1}^{A} \left\langle h_i \right| T \left| h_i \right\rangle + \frac{1}{2} \sum_{i,j=1}^{A} \left\langle h_i h_j \right| V \left| h_i h_j \right\rangle , \tag{11.46}$$

in terms of the occupied sp orbitals. Expanding the unknown occupied orbitals in terms of a fixed sp basis,

$$a^\dagger_{h_i} = \sum_\alpha z^*_{i\alpha} a^\dagger_\alpha , \tag{11.47}$$

the energy becomes

$$E = \sum_{i=1}^{A} \sum_{\alpha\beta} z^*_{i\alpha} z_{i\beta} \left\langle \alpha \right| T \left| \beta \right\rangle + \frac{1}{2} \sum_{i,j=1}^{A} \sum_{\alpha\beta\gamma\delta} z^*_{i\alpha} z^*_{j\beta} z_{i\gamma} z_{j\delta} \left\langle \alpha\beta \right| V \left| \gamma\delta \right\rangle . \tag{11.48}$$

This expression should be minimized with respect to variations in the expansion coefficients $z_{i\alpha}$, subject to the orthonormalization constraints for the occupied sp orbitals,

$$\sum_\alpha z^*_{j\alpha} z_{i\alpha} = \delta_{i,j} . \tag{11.49}$$

The condition for a constrained extremum reads

$$\frac{\partial}{\partial z^*_{i\alpha}} \left[E - \sum_{i,j=1}^{A} \epsilon_{ij} \sum_{\alpha} z^*_{j\alpha} z_{i\alpha} \right] = 0, \tag{11.50}$$

where the Lagrange multipliers ϵ_{ij} form a hermitian matrix. Working out the derivative yields the set of nonlinear equations

$$\sum_{\beta} \langle\alpha|\, T \,|\beta\rangle\, z_{i\beta} + \sum_{\beta\gamma\delta} \langle\alpha\beta|\, V \,|\gamma\delta\rangle\, (\sum_{j=1}^{A} z^*_{j\beta} z_{j\delta}) z_{i\gamma} = \sum_{j=1}^{A} \epsilon_{ij} z_{j\alpha}, \tag{11.51}$$

which should be solved together with the constraints in Eq. (11.49).

Without loss of generality we may assume the matrix ϵ_{ij} to be diagonal. If a solution is found where it is not, one can consider a unitary mixing of the z_i-vectors,

$$\begin{aligned} z_{i\alpha} &= \sum_{j=1}^{A} U_{ij} z'_{j\alpha}, \\ z'_{i\alpha} &= \sum_{j=1}^{A} U^*_{ji} z_{j\alpha}. \end{aligned} \tag{11.52}$$

The expression in Eq. (11.48) for the energy is invariant under such a transformation, so the set of $z_{i\alpha}$ is only determined up to a unitary transformation by the minimalization problem. The underlying solution, of course, is always the same, since the independent particle state in Eq. (11.45) does not change (apart from a global phase) under a unitary mixing of the occupied orbitals. Equation (11.51) transforms as

$$\sum_{\beta} \langle\alpha|\, T \,|\beta\rangle\, z'_{i\beta} + \sum_{\beta\gamma\delta} \langle\alpha\beta|\, V \,|\gamma\delta\rangle\, (\sum_{j=1}^{A} z'^*_{j\beta} z'_{j\delta}) z'_{i\gamma} = \sum_{j=1}^{A} \epsilon'_{ij} z'_{j\alpha}, \tag{11.53}$$

where

$$\epsilon'_{ij} = \sum_{k,l=1}^{A} U^*_{ki} \epsilon_{kl} U_{lj} = \left[U^\dagger \epsilon U \right]_{ij}. \tag{11.54}$$

From Eq. (11.54) it follows that U can be chosen such that $\epsilon'_{ij} = \delta_{i,j}\epsilon_i$ is diagonal. This is the so-called canonical representation of the HF basis, and with this choice Eq. (11.53) becomes identical to the HF equations (11.20) derived in Sec. 11.1.

The variational nature of the HF ground state has two important consequences. Firstly, the HF ground-state energy in Eq. (11.29) is always larger than the exact ground-state energy, as it is the minimal expectation value of the Hamiltonian with respect to a *restricted* class (the Slater determinants) of A-particle wave functions.

A second consequence is Brillouin's theorem, which can be formulated as

$$\left\langle \Phi_{HF}^{A} \right| \hat{H} a_p^\dagger a_h \left| \Phi_{HF}^{A} \right\rangle = 0, \tag{11.55}$$

where labels h (hole) denote HF sp states that are occupied in Φ_{HF}^{A} and labels p (particle) denote unoccupied sp states. Note that the Slater determinants

$$\left| \Phi_{ph}^{A} \right\rangle = a_p^\dagger a_h \left| \Phi_{HF}^{A} \right\rangle, \tag{11.56}$$

formed by replacing a hole with a particle state in the HF determinant, are called particle-hole (ph) excitations. Brillouin's theorem asserts that the HF ground state is stable with respect to such ph excitations, which can therefore be regarded as first approximations to the excited states of the A particle system. In order to prove the theorem it is sufficient to notice that small variations of the occupied HF orbitals $a_h^\dagger$ are by necessity of the form

$$\delta a_h^\dagger = \sum_p \eta_{ph} a_p^\dagger, \tag{11.57}$$

since they have to be orthogonal to all hole states. The corresponding variation in Φ_{HF}^{A} can therefore be written as

$$\left| \delta\Phi_{HF}^{A} \right\rangle = \delta \left\{ \prod_h a_h^\dagger \left| 0 \right\rangle \right\} = \sum_h \left(\delta a_h^\dagger \right) a_h \left| \Phi_{HF}^{A} \right\rangle = \sum_{ph} \eta_{ph} a_p^\dagger a_h \left| \Phi_{HF}^{A} \right\rangle. \tag{11.58}$$

Since the energy is extremal with respect to such variations, we have

$$0 = \left\langle \Phi_{HF}^{A} \right| \hat{H} \left| \delta\Phi_{HF}^{A} \right\rangle = \sum_{ph} \eta_{ph} \left\langle \Phi_{HF}^{A} \right| \hat{H} a_p^\dagger a_h \left| \Phi_{HF}^{A} \right\rangle, \tag{11.59}$$

for arbitrary coefficients η_{ph}, and the theorem in Eq. (11.55) results.

Alternatively, one can show (Exercise 11.7.1) by direct evaluation of the matrix element in second quantization that

$$\left\langle \Phi_{HF}^{A} \right| \hat{H} a_p^\dagger a_h \left| \Phi_{HF}^{A} \right\rangle = \left\langle p \right| T \left| h \right\rangle + \sum_{h'} \left\langle ph' \right| V \left| hh' \right\rangle$$

$$= \langle p | H_{HF} | h \rangle = 0, \tag{11.60}$$

where the zero result follows from the fact that $\hat{H}_{HF}$ is diagonal in the HF sp basis[2].

The interpretation of the HF energies ϵ_h of the occupied sp states follows from the observation (Exercise 11.7.2),

$$\epsilon_h = \left\langle \Phi_{HF}^A \right| \hat{H} \left| \Phi_{HF}^A \right\rangle - \left\langle \Phi_{HF}^A \right| a_h^\dagger \hat{H} a_h \left| \Phi_{HF}^A \right\rangle . \tag{11.61}$$

This is Koopman's theorem, which states that the ϵ_h can be identified as removal energies [see Eq. (11.23)], if one identifies the one-hole states $\left| \Phi_h^{A-1} \right\rangle = a_h \left| \Phi_{HF}^A \right\rangle$ as approximate eigenstates in the $A - 1$ system.

11.1.4 *HF in coordinate space*

We consider here a general system of spin-$\frac{1}{2}$ fermions in a local external sp potential $U(\boldsymbol{r})$ and interacting with a local and spin-independent tp potential $V(\boldsymbol{r}_1 - \boldsymbol{r}_2)$ (this is applicable to electrons in atoms or molecules). As the HF equations in Sec. 11.1.1 are valid in a general sp basis, the coordinate space representation is easily derived from Eq. (11.20) by taking sp labels $\alpha \equiv \boldsymbol{r} m_s$. We also introduce the more familiar wave-function form for the removal amplitude

$$z_{\boldsymbol{r} m_s}^n = \phi_n(\boldsymbol{r}, m_s). \tag{11.62}$$

Recalling [see Eq. (3.56)] the matrix elements of the kinetic energy operator in coordinate space, the first term in Eq. (11.20) becomes

$$\sum_{m_s'} \int d\boldsymbol{r}' \left\langle \boldsymbol{r} m_s \right| T \left| \boldsymbol{r}' m_s' \right\rangle \phi_n(\boldsymbol{r}', m_s') = -\frac{\hbar^2}{2m} \boldsymbol{\nabla}^2 \phi_n(\boldsymbol{r}, m_s). \tag{11.63}$$

The second term in Eq. (11.20) involves the tp interaction. For the present local and spin-independent tp interaction the direct matrix element is

$$\begin{aligned} &(\boldsymbol{r}_1 m_{s_1}, \boldsymbol{r}_2 m_{s_2} | V | \boldsymbol{r}_3 m_{s_3}, \boldsymbol{r}_4 m_{s_4}) = \\ &\quad \delta_{m_{s1}, m_{s3}} \delta_{m_{s2}, m_{s4}} \delta(\boldsymbol{r}_1 - \boldsymbol{r}_3) \delta(\boldsymbol{r}_2 - \boldsymbol{r}_4) V(\boldsymbol{r}_1 - \boldsymbol{r}_2). \end{aligned} \tag{11.64}$$

[2] Note that Brillouin's theorem does *not* imply that in general ph excitations are absent when expanding the exact ground state Ψ_0^A in a series of $1p1h$, $2p2h$,... excitations on the HF groundstate: they can still be mixed in through the coupling between $1p1h$ and $2p2h$ states.

Upon substitution, the HF equations (11.20) in coordinate space therefore read,

$$\begin{aligned} \epsilon_n \phi_n(\boldsymbol{r}, m_s) &= -\frac{\hbar^2}{2m} \boldsymbol{\nabla}^2 \phi_n(\boldsymbol{r}, m_s) \\ &+ \left[\int d\boldsymbol{r}' V(\boldsymbol{r} - \boldsymbol{r}') \sum_{m_s'} n^{HF}(\boldsymbol{r}' m_s', \boldsymbol{r}' m_s') \right] \phi_n(\boldsymbol{r}, m_s) \\ &- \sum_{m_s'} \int d\boldsymbol{r}' V(\boldsymbol{r} - \boldsymbol{r}') n^{HF}(\boldsymbol{r}' m_s', \boldsymbol{r} m_s) \phi_n(\boldsymbol{r}', m_s'), \end{aligned} \tag{11.65}$$

where

$$n_{HF}(\boldsymbol{r}' m_s', \boldsymbol{r} m_s) = \sum_{n=1}^{N} \phi_n(\boldsymbol{r}, m_s) \phi_n^*(\boldsymbol{r}', m_s') \tag{11.66}$$

is the HF one-body density matrix in coordinate space.

In Eq. (11.65) the first term involving the tp interaction is called the direct or Hartree contribution to the mean field. It can be written in terms of a local potential in coordinate space

$$v_H(\boldsymbol{r}) = \int d\boldsymbol{r}' n^{HF}(\boldsymbol{r}') V(\boldsymbol{r} - \boldsymbol{r}') \tag{11.67}$$

which represents the tp interaction averaged over the HF density,

$$n^{HF}(\boldsymbol{r}) = \sum_{m_s} n^{HF}(\boldsymbol{r} m_s, \boldsymbol{r} m_s). \tag{11.68}$$

The second term is the exchange or Fock contribution, and is obviously non-local in coordinate (and spin) space.

It may be surprising that the Hartree potential $v_H(\boldsymbol{r})$ contains the total density of the A particle system; in a mean-field picture one would expect a particle moving in orbital ϕ_n to interact with the $A-1$ other particles in orbitals ϕ_i $(i \neq n)$, and not with itself. In fact, the HF approximation is free from such spurious self-interaction, as can be seen by isolating in Eq. (11.65) the contribution from ϕ_n to the HF one-body density matrix: the Hartree and Fock terms cancel each other.

11.1.5 *Unrestricted and restricted Hartree-Fock*

At this point it is useful to analyze the spin dependence of the HF equations. The Hamiltonian we adopted has no spin dependence and obviously