PART A
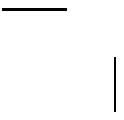# DFT: The Basic Workhorse

1 Principles of Density Functional Theory: Equilibrium and Nonequilibrium Applications

FERDINAND EVERS

Institute of Nanotechnology and Institut für Theorie der Kondensierten Materie, Karlsruhe Institute of Technology, Karlsruhe, Germany

Arguably, the most important method for electronic structure calculations in intermediate- and large-scale atomic or molecular systems is density functional theory (DFT). In this introductory chapter we discuss fundamental theoretical aspects underlying this framework. Our aim is twofold. First, we briefly explain our view on several aspects of DFTs as we understand them. Second, we discuss the fundamentals underlying applications of DFT to transport problems. Here, we offer a derivation of the salient equations which is based on single-particle scattering theory; the more standard approach relies on the nonequilibrium Green's function (or Keldysh) technique.

More practical aspects of applying DFT to large systems such as nanoparticles, liquids, large molecules, and proteins are described in Chapter 2 (using atomic basis sets) and Chapter 3 (using plane-wave basis sets). Other recent reviews of basic application procedures by Kümmel and Kronik[1] and Neese[2] are also available. Chapters 11 to 19 focus on applications, introducing extensions of the basis methods when required.

1.1 EQUILIBRIUM THEORIES

The interacting N-electron problem is a formidable challenge for the theoretical disciplines of physics and chemistry. It is formulated in terms of a Hamiltonian, $\hat{H}$, which has the general structure

$$\hat{H} = \sum_i [\varepsilon(\hat{\boldsymbol{p}}_i) + v_{\text{ex}}(\hat{\boldsymbol{r}}_i)] + \frac{1}{2} \sum_{ij} u(\hat{\boldsymbol{r}}_i - \hat{\boldsymbol{r}}_j) \qquad (1.1)$$

Here we have introduced the following notation: v_{ex} describes the system-specific time-independent external potential, which is generated, for example, due to the atomic nuclei. $\varepsilon(\mathbf{p})$ denotes the *dispersion* of the free particle, establishing the relation between the momentum of the particle and its energy in *free space* (i.e., in the absence of v_{ex} and the third term in u). For example, a single free particle with mass m has a dispersion $\varepsilon(\mathbf{p}) = \mathbf{p}^2/2m$. The third term introduces the two-particle interactions [e.g., $u(\mathbf{r}) = e^2/|\mathbf{r}|$ for the Coulomb case]. (We indicate an operator by $\hat{O}$ to distinguish it from its eigen- or expectation values.)

Density functional theory in its simplest incarnation serves to calculate several ground-state (GS) properties of this interacting many-body system. For example, one obtains the GS particle density, $n(\mathbf{r})$, the GS energy, E_0, or the workfunction (ionization energy), W. DFT owes its attractiveness to the fact that all of this can be obtained, in principle, by solving an optimization problem for the GS density alone without going through the often impractical explicit calculation of the GS wavefunction, Ψ_0, of the Hamiltonian (1.1). The actual task is to find a density profile, $n(\mathbf{r})$, so that the functional inside the brackets,

$$E_0 = \min_{\tilde{n}(\mathbf{r})} \left[F[\tilde{n}] + \int d\mathbf{r} v_{ex}(\mathbf{r})\tilde{n}(\mathbf{r}) \right] \qquad (1.2)$$

is invariant under small variations, $\delta\tilde{n}(\mathbf{r})$. Here F is a certain functional of the test density $\tilde{n}(\mathbf{r})$ that depends on the free dispersion, $\varepsilon(\mathbf{p})$, and the type of two-particle interactions, but not on the (static) environment, $v_{ex}(\mathbf{r})$. [The explicit definition of F is given in Eq. (1.10)]. The optimizing density coincides with the GS density and the optimum value of the functionals inside brackets delivers the GS energy.

1.1.1 Density as the Basic Variable

At first sight, the very existence of a formalism that allows us to obtain the GS properties mentioned without evaluating Ψ_0 itself may perhaps be surprising. After all, the particle density appears to involve a lot fewer degrees of freedom than Ψ_0, which is the canonical starting point for calculation of the expectation values of the observables. Indeed, $\Psi_0(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ is a complex field that depends on the individual coordinates of each of the N particles. By contrast, the density is an expectation value of the density operator:

$$\hat{n}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \hat{\boldsymbol{r}}_i) \qquad (1.3)$$

which may be obtained by integrating out most of the coordinates ("details") of Ψ_0:

$$n(\mathbf{r}) = \sum_i \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \; \delta(\mathbf{r} - \mathbf{r}_i)|\Psi_0(\mathbf{r}_1, \ldots, \mathbf{r}_N)|^2 \qquad (1.4)$$

$n(\mathbf{r})$ is a real field depending on a single coordinate only.

At a second glance, however, the essential concepts underlying DFT are quite naturally understood. From a certain perspective, most of the information content of the ground state Ψ_0 is redundant.

To see why this is a case, we discuss an example. Consider all thermodynamic properties of a system described by the Hamiltonian (1.1). Each property corresponds to calculating some ratio of expectation values:

$$O = \frac{\text{Tr}[\hat{O}e^{-\beta\hat{H}}]}{\text{Tr}[e^{-\beta\hat{H}}]} \tag{1.5}$$

with an inverse temperature, $\beta = 1/kT$, and $\hat{O}$ denoting the operator corresponding to the observable of interest. The important thing to notice is that the system characteristics enter the average only via $\hat{H}$. Therefore, *within a given set of systems with members sharing the same kinetic energy and two-body interaction* ("universality class"), *all system specifics* (i.e., *observables*) *are determined uniquely by specifying the external potential*, so O is a functional of v_{ex}: $O[v_{\text{ex}}]$. This simple observation already implies that within such a universality class, the system behavior can be reconstructed from knowledge of a scalar field [here $v_{\text{ex}}(\mathbf{r})$], and in this sense most of the information content of Ψ_0 is redundant.

In the Schrödinger theory, the classifying scalar field is the external potential. DFT amounts to a change of variables that replaces $v_{\text{ex}}(\mathbf{r}) \rightarrow n(\mathbf{r})$. Such a transformation is feasible because the density operator and the external potential v_{ex} enter $\hat{H}$ as a product, $\sum_{i=1}^{N} v_{\text{ex}}(\hat{\mathbf{r}}_i) = \int d\mathbf{r} v_{\text{ex}}(\mathbf{r})\hat{n}(\mathbf{r})$. Therefore, the average density and v_{ex} are *conjugate variables* and a relation

$$n(\mathbf{r}) = \frac{\partial E_0[v_{\text{ex}}]}{\partial v_{\text{ex}}(\mathbf{r})} \tag{1.6}$$

holds true. Under the assumption that Eq. (1.6) can be inverted (at least "piecewise"), we can employ a Legendre transformation to facilitate the change in variables from v_{ex} to n:

$$F[n] = E_0[v_{\text{ex}}] - \int d\mathbf{r}\, n(\mathbf{r})v_{\text{ex}}(\mathbf{r}) \tag{1.7}$$

where the external potential is now the dependent variable given by

$$v_{\text{ex}}(\mathbf{r}) = \frac{-\partial F[n]}{\partial n(\mathbf{r})} \tag{1.8}$$

Thus, it is suggested that the density n can also be considered the fundamental variable, so that observables are functionals thereof. The ground-state energy is an example of this.

Summarizing: Underlying DFT is the insight that within a given universality class, each physical system can be identified uniquely either by the belonging "environment," $v_{\text{ex}}(\mathbf{r})$, or by its GS density, $n(\mathbf{r})$. Therefore, in principle, knowing just the ground-state density is enough information to determine any observable (equilibrium) quantity of a many-body system.

Remarks

- A formal proof that the density can act as the fundamental variable was presented by Hohenberg and Kohn[3]; see Section 1.1.1.
- A generalization of DFT to spin or current DFT may be indicated for systems with degeneracies. Then additional fields such as magnetization and current density are needed to distinguish among the system states.

1.1.2   Variational Principle and Levy's Proof

Just the mere statement that equilibrium expectation values of observables can be calculated from some functionals once the GS density, n, is known, is not very helpful. For DFT to be self-consistent, also needed is a procedure to obtain this GS density by not referring to anything other than the functionals of n itself. This is where the variational principle kicks in, which says that the GS has a unique property in that it minimizes the system's total energy. This implies, in particular, that the GS has a density that minimizes (for a fixed environment v_{ex}) the functional $E_0[n]$. Hence, we can find n by solving the optimization problem (1.2), involving only variations of the density.

A particularly instructive derivation of Eq. (1.2) has been given by Levy.[4] We summarize the essential logical steps, to remind ourselves that the connection between the variational principle and DFT is actually deep and not related only to practical matters. In fact, Levy's proof starts with the variational principle for the GS. It implies that there is a configuration space, C, of totally anti-symmetric functions, $\tilde{\Psi}$, with the normalization property $N = \int d\mathbf{r} \, \langle \tilde{\Psi} | \hat{n}(\mathbf{r}) | \tilde{\Psi} \rangle)$, together with a functional $E[\tilde{\Psi}] = \langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle$ defined on this space, which is optimized by the GS, Ψ_0, with the GS energy, E_0, being the optimum value; explicitly,

$$E[\tilde{\Psi}] = \langle \tilde{\Psi} | \hat{T} + \hat{U} | \tilde{\Psi} \rangle + \int d\mathbf{r} \, v_{ex}(\mathbf{r}) \tilde{n}(\mathbf{r}) \tag{1.9}$$

where $\hat{T}$ abbreviates the kinetic energy and $\hat{U}$ the interaction energy appearing in Eq. (1.1), and $\tilde{n}$ is the particle density associated with $\tilde{\Psi}$. The trick in Levy's argument is to organize the minimum search in two steps. In the first step the total configuration space, C, is subdivided into subspaces such that all wavefunctions inside a given subspace have identical density profiles $\tilde{n} = \langle \tilde{\Psi} | \hat{n}(\mathbf{r}) | \tilde{\Psi} \rangle$. Next, within each subspace a search is launched for the elements that minimize E. Thus, a submanifold, M_{preopt}, is identified which contains a set of "preoptimized" elements. By construction, each element $\Psi_{\tilde{n}}$ of M_{preopt} is uniquely labeled by the associated density profile $\tilde{n}$ (see Fig. 1.1). In the second step, the minimum search is continued, but it can now be restricted to finding the one element, Ψ_0, of M_{preopt} that minimizes E.

The motivation behind this particular way of organizing the search is the following: The division procedure in step 1 has been constructed such that the second term in Eq. (1.9) does not contribute to preoptimizing; within a given
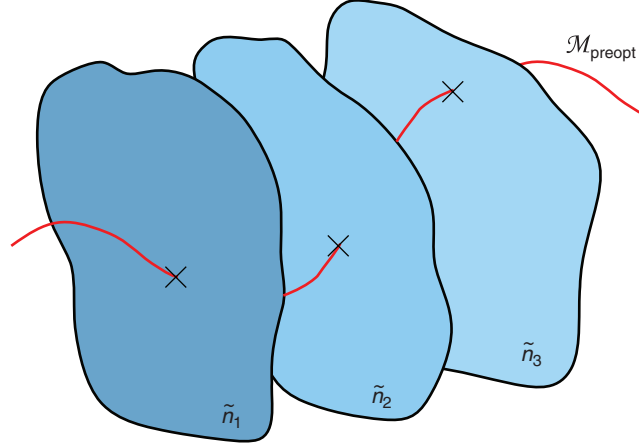
Fig. 1.1 (color online)   Schematic Al representation of the constraint search strategy in C space. One sorts the space of all possible (i.e., antisymmetrized, normalizable) wavefunctions into submanifolds. By definition, wavefunctions belonging to the same submanifold generate the same density profile, $\tilde{n}(\mathbf{r})$. Each submanifold has a wavefunction $\Psi[\tilde{n}(\mathbf{r})]$ (at fixed external potential v_{ex}), which has the lowest energy. These wavefunctions sit on a *hypersurface* (a "line") in the configuration space which is parameterized by $\tilde{n}(\mathbf{r})$. The surface is continuously connected if the evolution of $\Psi[\tilde{n}(\mathbf{r})]$ with the density profile is smooth (i.e., if degenerate shells with more than one optimum state Ψ do not exist). (We identify with each other states that differ only by a spatially homogeneous phase.) Typically, for every external potential, v_{ex}, there is exactly one such surface. The ground-state energy is found by going over the surface and searching for the global energy minimum.

subspace it is just a constant. In this step, only the first term is minimized, with an extremal value,

$$F[\tilde{n}] \equiv \langle \Psi_{\tilde{n}} | \hat{T} + \hat{U} | \Psi_{\tilde{n}} \rangle \tag{1.10}$$

The important observation is that by construction the functional $F[\tilde{n}]$ is universal (i.e., *independent of external conditions*, v_{ex}). (This statement is contained in the Hohenberg–Kohn theorem.[3]) Therefore, F is found by preoptimizing once and for all.

After F has been identified, the calculation of system-specific properties (depending on v_{ex}), which was described in Eq. (1.2), requires only a restricted search within the submanifold M_{preopt}. The benefit is tremendous, since the volume to be searched, M_{preopt}, is tiny compared to the original wavefunction space C.

Remarks
- $F[n]$ has the exact property

$$\left. \frac{\partial F[\tilde{n}]}{\partial \tilde{n}(\mathbf{r})} \right|_{\tilde{n}=n} + v_{ex}(\mathbf{r}) = \mu$$

Proof: The ground-state density, n, is an extremal point by construction under the constraint $N = \int d\mathbf{r}\,\tilde{n}(\mathbf{r})$. Introducing a Lagrange parameter, μ, we can release the constraint and perform an unrestricted search minimizing $F[\tilde{n}] + \mu N + \int d\mathbf{r}[v_{\text{ex}}(\mathbf{r}) - \mu]\tilde{n}(\mathbf{r})$. The claim follows after functional differentiation.

- The minimum search in Eq. (1.2) is in a space of scalar functions $\tilde{n}$, which have the property that they are "Ψ-representable": For a given $\tilde{n}(\mathbf{r})$ there is at least one element of C with the property $\tilde{n}(\mathbf{r}) = \langle\tilde{\Psi}|\hat{n}(\mathbf{r})|\tilde{\Psi}\rangle$. This implies, for example, positivity: $\tilde{n} \geq 0$.

- We presented Levy's argument for ground-state DFT. It is obvious, however, that the restriction to GS and the collective mode "density" was not crucial. Only the variational principle and a linear coupling of an environmental field to some collective mode (e.g., density, spin density, current density) should be kept. Therefore, generalizations of ground-state DFT to many other cases have been devised: for example, (equilibrium) thermodynamic DFT at nonzero temperature, magnetic properties (spin DFT and current DFT), and relativistic DFTs.

  Moreover, it has been shown that certain excited states can also be calculated exactly with a ground-state (spin) DFT. This happens when the Hamiltonian, $\hat{H}$, exhibits symmetries, such as spin rotational invariance. Then the Hilbert space decomposes into invariant subspaces each carrying its own quantum number(s), q: for example, a spin multiplicity. The minimum search may then proceed in every subspace, separately, giving a separate functional F_q for each of them. The local q-minima thus obtained are valid eigenstates of the full Hamiltonian (Gunnarsson–Lundqvist theorem[5]).

1.2 LOCAL APPROXIMATIONS

The precise analytical dependency of the energy functional $F[n]$ on the density $n(\mathbf{r})$ is not known, of course. Available approximations employ knowledge, analytical and computational, about *homogeneous* interacting Fermi gases (i.e., the case $v_{\text{ex}} = \text{const}$). Indeed, it turns out that the homogeneous system also provides a very useful starting point to build up a zeroth-order description in the inhomogeneous environments that are relevant for describing atoms and molecules.

1.2.1 Homogeneous Electron Gas

Homogeneous gases are relatively simple. The particle density, n, is just a parameter and all functionals, which in general involve multiple spatial integrals over expressions involving $n(\mathbf{r})$ at different positions in space (nonlocality property), turn into functions of n. Analytical expressions for them can usually be derived from perturbative treatments of $E_0(n)$, which are justified in two limiting cases: where a control parameter, r_s, is either very large or very small.

For the homogeneous electron gas, r_s can easily be identified: It is the ratio of two energies. The first energy is the typical strength of the interaction that two

particles feel in the electron gas in three-dimensional space: $(e^2/\varepsilon_0)n^{1/3}$. To see whether or not this energy is actually sizable, one should compare it to another energy. The correct energy scale to consider will be a measure of the kinetic energy of the particles.

The average kinetic energy of a fermion depends on the gas density, n. To derive an explicit expression, we recall that due to the Pauli principle, all particles that share the same spin state must be in different momentum states, $|\mathbf{p}\rangle$. Therefore, when filling up the volume, higher and higher momentum states, up to a maximum momentum value, p_F, will be occupied. The kinetic energy of the particles occupying the highest-energy (*Fermi energy*) states, $\varepsilon_F(n) \equiv \varepsilon(p_F)$, will be a good measure for the typical kinetic energy of a gas particle.

The situation is best visualized recalling the familiar quantum mechanical textbook problem of "a particle in a box" with box size L. The energy levels of the box can be ordered according to the number of nodes exhibited by the corresponding wavefunctions. The spatial distance between two nodes gives half the wavelength, $\lambda/2$, with an associated wavenumber $k = 2\pi/\lambda$ and momentum $p = \hbar k$. The maximum wavelength reached by N particles (with spin $\frac{1}{2}$) filling the box is $\lambda_F/2 = L/(N/2) = 2/n$, giving rise to a maximum wavenumber, the *Fermi wavenumber* $k_F = \pi n/2$, and a maximum momentum $p_F = \hbar k_F$. In three dimensions, similar considerations yield $\pi k_F^3/3 = (2\pi)^3(n/2)$.

Employing these results, our dimensionless parameter can now be specified as $r_s \sim e^2 n^{1/3}/\varepsilon_0 \varepsilon_F(n)$, which conventionally is cast into the form

$$\frac{4\pi}{3}r_s^3 = \frac{1}{na_0^3}$$

stipulating a parabolic dispersion $\varepsilon(p) = p^2/2m$ (ε_0: effective dielectric constant; $a_0 = 4\pi\varepsilon_0\hbar^2/me^2 \approx 0.529$ Å: Bohr's radius). Analytical expansions of $E_0(n)$ are available in the limiting cases $1/r_s \ll 1$ or $r_s \ll 1$. Typically, in particular with molecular systems, one has the marginal case $r_s \simeq 1$. Here, computational methods such as quantum Monte Carlo calculations (see Chapter 4) help to interpolate the gap.

Motivated from the weakly interacting limit ($r_s \ll 1$), conventionally we consider the following splitting of the GS energy per unit volume[†]:

$$\breve{\varepsilon}_0(n) = 2 \sum_{|\mathbf{k}| \leq k_F(n)} \varepsilon(\mathbf{k}) + v_{XC}(n) \tag{1.11}$$

[†]For homogeneous densities, the Hartree term reads $n \int d\mathbf{r}'\, u(\mathbf{r} - \mathbf{r}')$. Since the spatial summation over the Coulomb potential, $\sim 1/r$, does not converge, the integral makes a contribution to the energy balance which is formally infinite. This divergency is an artifact of modeling the interacting electron gas without taking into consideration the (positive) charge of those atomic nuclei ("counter charges") that provide the source of the electrons to begin with. The physical system is always (close to) charge neutral, so that (on average) $n_{nuclei} = -n_{electrons}$. This implies that the nuclei provide a "background" potential, $n_{nuclei} \int d\mathbf{r}'\, u(\mathbf{r} - \mathbf{r}')$, that leads to an exact cancellation of the divergent contribution in the Hartree term. Therefore, this particular term should be ignored when dealing with the homogeneous electron system (the Jellium model).

where the factor of 2 accounts for the electron spin. The first term comprises the kinetic energy of the free gas. Its dependency on the density is regulated via the Fermi wavenumber, $k_F(n)$. The second term includes the remaining correlation effects and therefore has a weak coupling expansion. For the Coulomb case, the leading term is $\sim 1/r_s$ with subleading corrections,[6]

$$v_{XC}(n) = -n \frac{0.9163}{r_s} + n[-0.094 + 0.0622 \ln r_s + 0.018 r_s \ln r_s + O(r_s)] \quad (1.12)$$

in Rydberg units ($E_{Ry} = E_{Hartree}/2 \approx 13.6$ eV).

1.2.2 Local Density Functional

The information taken from homogeneous systems for constructing functionals describing inhomogeneous systems is the dependency of the GS energy per volume on the particle density, $\breve{\varepsilon}_0(n)$. A leading-order approximation for the general F-functional is obtained by

$$F[n] = \int d\mathbf{r} \breve{\varepsilon}_0(n(\mathbf{r})) \quad (1.13)$$

This approximation is valid if the inhomogeneous system is *real-space separable*, meaning that it can be decomposed into a large number of subsystems that (1) still contain sufficient particles to allow for treatment as an electron gas with a finite density, (2) are already small enough to be nearly homogeneous in density, and (3) have negligible interaction with each other. Systems exhibiting a relative change of density, which is large even on the shortest length scale available, the Fermi wavelength λ_F, do not satisfy (1) and (2) simultaneously. So a minimal condition for the applicability of Eq. (1.13) is

$$\frac{\lambda_F \nabla n}{n \ll 1} \quad (1.14)$$

Remarks
- Condition (3) implies that the interaction is short range, ideally $u(\mathbf{r} - \mathbf{r}') \sim \delta(\mathbf{r} - \mathbf{r}')$. For the Coulomb case, we separate from the $1/|\mathbf{r} - \mathbf{r}'|$-interaction a long-range term, which is then treated by introducing an extra term, the Hartree potential.
- Since the Fermi wavelength itself depends on the density, $\lambda_F \sim n^{-1/d}$, relation (1.14) is satisfied typically only in the large n-limit. There, the main contribution to the energy (1.13) stems from the kinetic term in Eq. (1.11). Therefore, the leading error in the local functional (1.14) usually comes from the fact that the *Thomas–Fermi approximation* $[k_F(\mathbf{r}) \equiv k_F(n(\mathbf{r}))]$

$$\langle \hat{T} \rangle \approx 2 \int d\mathbf{r} \sum_{|\mathbf{k}| \leq k_F(r)} \varepsilon(\mathbf{k}) \quad (1.15)$$

gives only a very poor estimate of the kinetic energy of an inhomogeneous electron gas, even for noninteracting particles.

• The failure of the Thomas–Fermi approximation is the main reason that orbital-free DFT has a predictive power too limited for most practical demands. The search for more accurate representations of the kinetic energy in terms of n-functionals is at present an active field of research.[7,8]

1.3   KOHN–SHAM FORMULATION

Better estimates for the kinetic energy can be obtained within the *Kohn–Sham formalism*.[9] One addresses the optimization problem (1.2) by reintroducing an orbital representation of the density with single-particle states,

$$n(\mathbf{r}) = \sum_{\ell=1}^{\tilde{N}} |\phi_\ell(\mathbf{r})|^2 \tag{1.16}$$

called the *Kohn–Sham* or *molecular orbitals*. The orbitals ϕ_ℓ are sought to be ortho-normalized; the parameter $\tilde{N}$ is free, in principle. However, with an eye on approximating the kinetic energy of the interacting system by the energy of the free gas, $\tilde{N}$ is usually chosen to be equal to the number of particles, $\tilde{N} = N$. With this choice, the optimization problem formally reads

$$\frac{1}{2}\frac{\partial}{\partial\phi_\ell^*(\mathbf{r})}[E_0[n(\mathbf{r})] - \varepsilon_\ell(\langle\phi_\ell|\phi_\ell\rangle - 1)] = 0 \tag{1.17}$$

featuring the *Kohn–Sham energies* (or *molecular orbital energies*), ε_ℓ, which play the role of Lagrange multipliers ensuring normalization. Equation (1.17) can be cast conveniently into a form reminiscent of a Schrödinger equation of N single particles:

$$[\varepsilon(\mathbf{p}) + v_s(\mathbf{r})]\phi_\ell(\mathbf{r}) = \varepsilon_\ell\phi_\ell(\mathbf{r}) \tag{1.18}$$

where we have employed a substitution ($\mathbf{p} = -i\hbar\partial_x$),

$$\frac{1}{2}\frac{\partial}{\partial\phi_\ell^*(\mathbf{r})}E_0[n(\mathbf{r})] = [\varepsilon(\mathbf{p}) + v_s(\mathbf{r})]\phi_\ell(\mathbf{r}) \tag{1.19}$$

which is merely a definition of an auxiliary quantity, the effective potential $v_s(\mathbf{r})$. The set of N equations given by Eq. (1.18) constitutes the *Kohn–Sham equations*.

Remarks

• The Kohn–Sham (KS) formalism should give a much improved description of the kinetic energy, because by construction it reproduces exactly the kinetic energy of the inhomogeneous, noninteracting gas.

- The fictitious KS particles live in an effective potential which modulates their environment such that their density and all related properties coincide with those of a true many-body system.
- The potential term has a decomposition

$$v_s(\mathbf{r}) = v_{ex}(\mathbf{r}) + v_H(\mathbf{r}) + v_{XC}(\mathbf{r}) \qquad (1.20)$$

where the second term includes the Hartree interaction, which for a specific two-body interaction potential $u(\mathbf{r} - \mathbf{r}')$ reads $v_H(\mathbf{r}) = \int d\mathbf{r}'\, u(\mathbf{r} - \mathbf{r}')n(\mathbf{r}')$. The third term, the *exchange–correlation potential*, incorporates all the remaining, more complicated many-body contributions. In particular, we have also lumped the difference between the free and interacting kinetic energies into this term.

- Solving the KS equations requires diagonalization of a *KS-Hamiltonian*:

$$\hat{H}_{KS} = \varepsilon(\hat{\boldsymbol{p}}) + v_s(\hat{\boldsymbol{r}}) \qquad (1.21)$$

The dimension of the corresponding Hilbert space, N_ϕ, usually exceeds the particle number substantially: $N_\phi \gg N$. Therefore, occupied (real) eigenstates that finally enter the construction of the density [Eq. (1.16)] need to be distinguished from unoccupied (virtual) ones. The selection process follows the variational principle.

- Similar to the Hartree theory and in pronounced contrast to the Schrödinger equation for a single particle, the KS equations pose a self-consistency problem: The potential $v_s(\mathbf{r})$ is a functional of $n(\mathbf{r})$, so it needs to be determined "on the fly." We emphasize that even though the functional $v_s[n](\mathbf{r})$ may exhibit a very complicated—in particular, *nonlocal*—dependency on the ground-state particle density, the effective potential that finally is felt by the KS particles is perfectly local in space. It provides an effective environment for the KS particles, so that the many-body density can be reproduced.

- The self-consistent field (SCF) problem in DFT is much easier to solve than the Hartree–Fock (HF) equations, which are nonlocal in space and, what is much worse, even orbital dependent. As a consequence of the orbital dependency of the Fock operator, a real HF orbital interacts with $N - 1$ other real orbitals, whereas a virtual orbital interacts with N real orbitals. The situation in DFT is much simpler in the sense that occupied and unoccupied orbitals all feel the same effective potential $v_s[n](\mathbf{r})$. Notice, however, that this computational advantage comes at the expense of the *derivative discontinuity*, an unphysical feature of exact exchange correlation functionals (see Section 1.5.3) that is very difficult to implement in efficient approximation schemes.

- Our derivation of the Kohn–Sham equations was tacitly assuming the following: The density of *any* electron system, including the interacting systems, can be represented in the manner of Eq. (1.16), where the orbitals

ϕ_ℓ are normalizable solutions of a (single-particle) Schrödinger equation. Is this really true? The answer is: Not always. That is, systems with degenerate ground states may exhibit a particle density that can only be represented as a sum of independent contributions coming from a number g of single Slater determinants. A general statement that is valid for all practical purposes is that any fermionic density may be represented uniquely as a weighted average of g degenerate ground-state densities of some effective single-particle Schrödinger problem [Eq. (1.18)].[10,11]

1.3.1 Is the Choice of the KS–Hamiltonian Unique?

For an interacting many-body system, splitting between kinetic and potential energy as suggested in Eqs. (1.19) and (1.20) is not as unique as it may appear at first sight. To give a straight argument, recall that the dispersion relation of the free particles, $\varepsilon(\mathbf{p})$, can be altered substantially by interaction effects. For example, the mass of the electron describes how the particle's energy depends on its momentum. In the presence of interactions, an electron always moves together with its own screening cloud, brought about by the presence of other electrons. Although this does not change the wavelength (i.e., the momentum) of the electron, it does change its velocity. It tends to make it slower, so that the "effective" mass increases. Such interaction effects on parameters such as the mass, the thermodynamic density of states, and the magnetic susceptibility are called *Fermi-liquid renormalizations*.

Having this in mind, one could easily imagine another splitting featuring a *renormalized* kinetic energy, $\varepsilon^*(\mathbf{p})$, which would describe a more adapted description of the dispersion of charged excitations (e.g., the propagation of screened electrons) in the interacting quantum liquid.[12] A remaining, *residual interaction*, $V_{\text{XC}}^{\text{res}}$, would appear to be designed so that the ground-state density produced by this effective system would also coincide with the true density. Such a renormalized splitting is rarely employed in practice, perhaps because a good approximation for the residual functionals is not available.

For the effective single-particle problem that yields the exact ground-state density, we conclude that various choices are possible, the choices differing from one another in the dispersion $\varepsilon(\mathbf{p})$ that enters the kinetic part of the KS-Hamiltonian. Very few restrictions on the possible functional forms of $\varepsilon(\mathbf{p})$ exist; the parabolic shape and the trivial form $\varepsilon \equiv 0$ (with proper readjustments of v_{XC}) are just two choices out of many.

1.4 WHY DFT IS SO SUCCESSFUL

The precise dependency of the exchange–correlation potential v_{XC} on the density $n(\mathbf{r})$ is not known. In the simplest approximation, the *local density approximation* (LDA), one takes for v_{XC} the result obtained from the homogeneous electron gas [Eq. (1.12)], but replacing the homogeneous density with $n(\mathbf{r})$ (see Section 1.2.2).

Remarks

- The universal success of DFT in chemistry and condensed matter physics came with the empirical finding that the combination of KS theory with LDA (and its close relatives) works in a sufficiently quantitative way to make it possible to calculate ground-state energies (and hence to determine molecular and crystal structure) even *outside* the naive regime of the validity of LDA as given by relation (1.14). This is due to a cancellation of errors in the kinetic and exchange correlation part of the KS-Hamiltonian (1.21).[13]

- In analogy with Hartree–Fock theory, a fictitious "KS–ground state" wavefunction, Φ, is often considered. It is constructed by building a Slater determinant from the real KS orbitals. In contrast to HF, this state is *not* optimal in an energetic sense. It does, however, reproduce the exact particle density. In the same spirit, KS energies are often interpreted as single-particle energies, even though from a dogmatic point of view there is no (close) connection between the Lagrange multipliers and the true many-body excitations; indeed, to the best of our knowledge, a precise justification of this practice has never been given. Still, the pragmatic approach has established itself widely, since it often gives semiquantitative estimates for Fermi-liquid renormalizations, which are important, for example, in band structure calculations.

- The implementation of efficient codes is much easier in DFT than in HF theory, due to the fact that functionals are only density and not orbital dependent. For this reason, many powerful codes are readily available in the marketplace.

- At present, because of the virtues noted above, DFT is by far the most widely used tool in electronic structure theory (lattice structures, band structures) and quantum chemistry (molecular configurations), with further applications in many other fields, such as nuclear physics, strongly correlated systems, and material science.

1.5   EXACT PROPERTIES OF DFTs

Since there is no analytic solution of the general interacting many-body problem, it is not surprising that exact statements about exchange correlation functionals are scarce. Precise information is, however, available in the presence of an interface to the vacuum.

Imagine a situation in which a molecule or a piece of material is embedded in a vacuum. The material is associated with an attractive KS potential "well," v_s, which binds N electrons to the nuclei (or atomic ion cores). Outside the material, the binding potential and the particle density rapidly approach their asymptotic zero values. Exact information is available about how the asymptotic value is approached.

1.5.1 Asymptotic Behavior of v_{XC}

Consider the Hartree term

$$v_H(\mathbf{r}) = \sum_{\ell'=1}^{\text{occ}} \int d\mathbf{r}'\, u(\mathbf{r} - \mathbf{r}')|\phi_{\ell'}(\mathbf{r}')|^2 \tag{1.22}$$

in the KS equations

$$[\varepsilon(\hat{\boldsymbol{p}}) + v_{ex}(\mathbf{r}) + v_H(\mathbf{r}) + v_{XC}(\mathbf{r})]\phi_\ell(\mathbf{r}) = \varepsilon_\ell\phi_\ell(\mathbf{r}) \tag{1.23}$$

It contains at $\ell' = \ell$ a piece $u(\mathbf{r} - \mathbf{r}')|\phi_\ell(\mathbf{r}')|^2$, which incorporates an interaction of a particle in the occupied orbital ϕ_ℓ with its own density. This spurious, nonphysical interaction is known as a *self-interaction error*. In principle, it should be eliminated by an counterpiece contained in the exchange part of v_{XC}.[†] The construction and application of empirical corrections for this effect are the subject of Chapter 14.

The Hartree term is known exactly in the asymptotic region. This is the reason that it is possible to draw a rigorous conclusion about v_{XC}. To be specific, we consider the case of Coulomb interactions. In the asymptotic regime a distance r away from the materials center, where the particle density is totally negligible, all spurious contributions made by an occupied orbital add up to e^2/r. To cancel this piece we must have

$$v_{XC}(r) \underset{r\to\infty}{\to} -\frac{e^2}{r} + \frac{-\alpha_{N-1}}{2r^4} + \cdots \tag{1.24}$$

whenever the particle density vanishes. The correction term, which we have also given here, describes the polarizability, α_{N-1}, of the many-body system (with $N-1$ particles). This term incorporates the interactions with the fluctuating charge density of the mother system that particles feel when they explore the asymptotic region.

[†]This cancellation may be seen explicitly within the Hartree–Fock approximation. That is, the interaction term reads

$$\sum_{\sigma'=\uparrow,\downarrow} \sum_{\ell'} \int d\mathbf{r}'\, u(\mathbf{r} - \mathbf{r}')\phi^*_{\ell'\sigma'}(\mathbf{r}')[\phi_{\ell'\sigma'}(\mathbf{r}')\phi_{\ell\sigma}(\mathbf{r}) - \delta_{\sigma\sigma'}\phi_{\ell'\sigma'}(\mathbf{r})\phi_{\ell\sigma}(\mathbf{r}')]$$

so that the piece with $l' = l$, $\sigma' = \sigma$ in the first (Hartree) term is eliminated by a corresponding piece in the second (Fock) term.

Remarks

- A more intuitive way to rationalize the leading asymptotics of v_{XC} is to recall that an electron that makes a virtual excursion from its host material into vacuum still interacts with the hole that it leaves behind. The first term in Eq. (1.24) describes the interaction with this virtual hole.

- Both terms appearing in Eq. (1.24) are not recovered in local approximation schemes, such as LDAs and generalized-gradient approximations (GGAs), which stipulate the form $v_{XC}(\mathbf{r}) \approx v_{XC}(n(\mathbf{r}), \nabla n(\mathbf{r}), \ldots)$. The statement is obvious, because the density is exponentially small in the asymptotic region (see Section 1.5.2), whereas the potential (1.24) is not. This defect has very serious consequences, since the van der Waals dispersion interactions, $v_{XC} \sim -\alpha_{N-1}/r^4$, ignored in LDAs and GGAs, provide the dominating intermolecular forces that prevail, for example, in biochemical environments. To address this problem, Grimme[14] has proposed an ad hoc empirical procedure that adds a long-range term to standard energy functionals. The functional contains specific parameters, essentially modeling the local polarizability of single atoms or molecular groups chosen so that a rough description of the van der Waals interaction is retained.

1.5.2 Workfunction

Now, consider the KS potential well in its ground state with N occupied bound orbitals ϕ. Generically, every such orbital contributes to the particle density $n(\mathbf{r})$ at a point $\mathbf{r}$ unless it happens that ϕ has a node there: $\phi(\mathbf{r}) = 0$. This is also true in the asymptotic region far away from the well's center. However, in this region the state ϕ_{HOMO} with the largest KS energy [highest occupied molecular (or material) orbital (HOMO)] gives the dominating contribution almost everywhere (i.e., at all points where $|\phi_{HOMO}(\mathbf{r})|^2 > 0$). It is easy to see why this is. In the asymptotic region $v_s(\mathbf{r})$ decays in a power-law manner with the distance r from the well's center (Fig. 1.2). Therefore, the KS equations read

$$-\frac{\hbar^2}{2m}\partial_r^2(r\phi_\ell) = \varepsilon_\ell(r\phi_\ell) \tag{1.25}$$

where $\varepsilon_\ell < 0$ denotes the ionization energy of a bound KS state. The solution is

$$\phi_\ell \sim \frac{1}{r}e^{-\sqrt{2m|\varepsilon_\ell|/\hbar^2}\,r} \tag{1.26}$$

so that generically the HOMO orbital has the smallest KS energy by modulus, $|\varepsilon_{HOMO}|$. At large enough distances, it will give the only relevant contribution. [Exceptions to the rule occur only in the case of a vanishing prefactor not written in Eq. (1.26).] For this reason, the KS energy of the highest occupied molecular level is actually a physical observable; it gives the ionization energy or *workfunction* (Janak's theorem[15,16]).
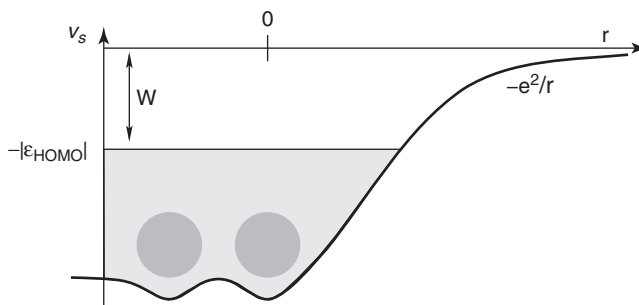
Fig. 1.2 Effective potential (solid line) near a surface of a simple metal. Surface atoms (dark balls) and the electron liquid (light background) are also indicated.

1.5.3 Derivative Discontinuity

The derivative discontinuity[17,18] (DD) is perhaps one of the less intuitive properties that an exact XC potential must exhibit. We discuss it here in some detail, since the fact that local approximations are not capable of capturing it even qualitatively often leads to very important artifacts in the KS spectra which are not a genuine feature of DFT itself but, rather, of the LDA.

We will see that the DD is related intimately to the fact that the N (real) particles in a many-body system interact with only $N-1$ partners, while an infinitesimal test (virtual) charge in such a system would interact with N (i.e., *all* the other particles). Since $v_{XC}[n]$ has access to the total density only, it cannot easily distinguish real and virtual orbitals with their different interacting environments (as HF does). It turns out that the way DFT implements such behavior is via a very sharp (i.e., nonanalytic) behavior of $v_{XC}[n]$ on the particle density $n(\mathbf{r})$.

1.5.3.1 Isolated System   Consider an isolated quantum dot, such as a single atom or a molecule, with N electrons. The corresponding KS system exhibits a number of N KS particles that occupy the N lowest-lying KS states. It is important to recall that each KS particle interacts with the *total* charge density, $v_{XC}[n_N]$, only, including the density contribution that comes from itself. In this respect, KS particles are fundamentally different from physical particles, which do not interact with themselves, of course.

Next, add one additional particle, the *excess charge*, $\delta N = 1$; to be specific, put it into the lowest unoccupied molecular orbital (LUMO^N). The new XC functional of the "anion" will be $v_{XC}[n_{N+1}]$. What are the consequences of charging for the KS energies? Due to the change $n_N \rightarrow n_{N+1}$, every original particle interacts with one more charge, δN, the excess particle in the LUMO^N. Therefore, the energy of every one of the first N orbitals shifts by the amount U, which measures the interaction with the excess particle (see Fig. 1.3). Notice also that the energy of the LUMO^N (now, better, HOMO^{N+1}) has shifted by U after it was occupied. This is because in KS theory, all orbitals, occupied and unoccupied, are calculated in *the same* effective potential.
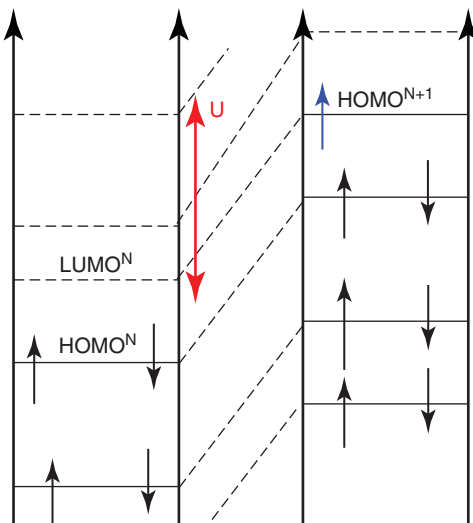
Fig. 1.3 Evolution of the energy of KS-frontier orbitals with increasing electron number from N (left) to $N + 1$ (right). The KS-LUMO^N jumps upon occupation by an amount U. By contrast, in Hartree–Fock (HF) energy the HF-LUMO^N is already calculated anticipating an interaction with one more particle (as compared to HF-HOMO^N). Therefore, such a jump does not occur in HF theory.

So far, no peculiarities have appeared. To see that there is indeed something looming on the horizon, now add a fractional excess charge, say an infinitesimally small one, $\delta N \lll 1$, rather than an integer charge. Then the original KS orbitals should remain invariant by definition, since the perturbation is infinitesimally small so that the charge density is not disturbed. But, what are the energy and shape of the newly occupied orbital? The salient point is that a real particle does not interact with itself. Therefore, the energy of a physical orbital should not be sensitive to its occupation. Hence, the workfunction of an atom with a fractionally occupied HOMO is the same as that of one with an integer occupation.

We conclude that the fractionally occupied orbital must have the energy HOMO^{N+1}, which exceeds the energy of the empty orbital LUMO^N by the amount U. So evolution of the energy of HOMO$^{N+\delta N}$ with δN is *not* smooth; an arbitrarily small change in the density, δN, must result in a finite reaction of $v_{XC}[n]$ if the particle number, N, is near integer values:

$$\Delta_{XC}(\mathbf{r}) = \left.\frac{\delta E_{XC}[n]}{\delta n(\mathbf{r})}\right|_{N+\delta N} - \left.\frac{\delta E_{XC}[n]}{\delta n(\mathbf{r})}\right|_{N-\delta N} \tag{1.27}$$

This is the (in)famous *derivative discontinuity* (DD).

1.5.3.2 Coupled Subsystems (Partial Charge Transfer) To illustrate the importance of the DD, we now give a typical example where fractional charge occurs.

Consider two subsystems, which are partially decoupled in the sense that electronic wavefunctions interact only weakly. Such could be, for example, two functional groups in the same molecule or two neighboring molecules in a biological environment. To be specific, we imagine here the atom from Section 1.5.3.1 and a second many-body system, a metal surface.

Each system has its own workfunction: for example, $W_A^{N+1} > W_S$. Let us bring the atom into the vicinity of the surface, but keeping their distance d extremely large. Since only the total particle number $N = N_A + N_S$ is conserved, there will be a net exchange of charge, δN, between $S \to A$. This implies that the atomic orbitals acquire a finite broadening, Γ, which however is small, $\Gamma \ll |W_A^{N+1} - W_S|$, since d is large. In this situation and in the absense of ionization, the net particle flow from $S \to A$ is exponentially small. As a consequence, the HOMO_A^{N+1} fills up, but only with a very small fraction of an electron.

To describe correctly how the HOMO_A^{N+1} fills upon approach of the two subsystems, it is crucial that the piece of the XC functional describing A indeed reacts to the flow, so that the LUMO_A^N of the coupled atom is shifted upward against the uncoupled atom by U. If U is on the order of the mean level spacing or even bigger—as it tends to be for nanoscopic systems such as atoms and small molecules—this shift is important for understanding charge transfer in DFT. On a qualitative level, the DD suppresses charge fluctuations between weakly coupled subsystems.

Remarks

- The spatial modulation of v_{XC} induced by the DD reflects the differences in the workfunction seen in different charge states of the isolated subsystems before they have been coupled. Therefore, quantitative estimates about the size of the DD-induced modulations can be obtained by calculating workfunctions of the constituting subsystems and their anions/cations.

- The DD enters in a crucial way the DFT-based description of the gate dependence of the charge inside a quantum dot. Without DD, the width of the Coulomb oscillations is U rather than $\max(\Gamma, T)$ and therefore qualitatively wrong.[19]

- In LDA-type approximations the DD is missing, since by construction the potentials evolve smoothly when an infinitesimal probing charge is added. Currently, attempts are under way to design orbital-dependent functionals which can take the DD into account (in a spirit similar to HF theory). Kümmel and Kronik[1] have compiled a review about the most recent developments in this direction.

1.6   TIME-DEPENDENT DFT

Since the 1980s, attempts have been made to generalize equilibrium theory into time dependent phenomena. A detailed account of its foundations may be found in recent monographs.[20,21] We discuss only those most basic aspects which are

important to shed some light on the connection between TDDFT and transport calculations.

Consider the time-dependent Schrödinger equation

$$i\hbar\partial_t\Psi(t) = \left[\hat{T} + \hat{U} + \hat{V}_{\text{ex}} + \int d\mathbf{r}\,\phi_{\text{ex}}(\mathbf{r}t)\hat{n}(\mathbf{r})\right]\Psi(t) \qquad (1.28)$$

where $\hat{T}$ and $\hat{U}$ abbreviate the kinetic and interaction energies given explicitly in Eq. (1.2) and, again,

$$\hat{V}_{\text{ex}} = \int d\mathbf{r}\,v_{\text{ex}}(\mathbf{r})\hat{n}(\mathbf{r})$$

describes the electrostatic environment. The time evolution of all observables is fixed by (1) the time-dependent external potential $\phi_{\text{ex}}(\mathbf{r}t)$ and (2) the initial conditions (i.e., the wavefunction Ψ_i at the initial time $t = 0$). This suggests that the response of all those systems, which have been prepared in an identical way and therefore share the same initial state, is dictated by a single scalar field $v_{\text{ex}}(t)$. In this respect, the situation is very reminiscent of the equilibrium case.

To prove also that for time-dependent phenomena the density may serve as the fundamental variable, one should demonstrate that an invertible relation analog to Eq. (1.6) exists, at least in principle, which allows reconstruction of the probing potential $\phi_{\text{ex}}(t)$ from knowledge of $n(t)$ (and Ψ_i) at all times $t \geq 0$. A proof that this indeed is the case for a wide class of potentials $\phi_{\text{ex}}(t)$ was constructed first by Runge and Gross[22] and corroborated by many later authors, in particular by van Leeuwen.[23]

1.6.1 Runge–Gross Theorem

The Runge–Gross theorem emphasizes that the time evolution of the density $n(t)$ is a *unique* characteristic of the probing potential $\phi_{\text{ex}}(t)$: Two probing fields, which differ by more than a homogeneous shift in space, invoke two different density evolutions. This insight is then later used to argue that a density profile, $n(\mathbf{r}t)$, that is driven in one system with interaction $\hat{U}$ by $\phi_{\text{ex}}(t)$ can also be seen in another system with a different interaction $\hat{U}'$ after $\phi_{\text{ex}}(t)$ has been replaced by the appropriate modulation $\phi'_{\text{ex}}(t)$. In particular, $\hat{U}'$ can also be zero, which is the foundation of the time-dependent DFT.

We offer a proof of these statements which relies on the familiar fact that a solution of a partial differential equation (here in time) is unique once the initial situation and the evolution law have been specified.

Proof The strategy is to relate the probing field ϕ_{ex} to the second time derivatives $\ddot{n}$. For the first time derivative, Heisenberg's equation of motion tells us that

$$\dot{n}(\mathbf{r}t) = \frac{1}{i\hbar}\langle\Psi(t)|[\hat{n}(\mathbf{r}),\hat{T}]|\Psi(t)\rangle \qquad (1.29)$$

because all other terms in $\hat{U}$, $\hat{V}_{\mathrm{ex}}$, and ϕ_{ex} commute with the density operator $\hat{n}(\mathbf{r})$. By comparing with the continuity equation,

$$\dot{n}(\mathbf{r}t) + \partial_{\mathbf{r}}\langle\Psi(t)|\hat{\boldsymbol{j}}(\mathbf{r})|\Psi(t)\rangle = 0 \tag{1.30}$$

one may identify the proper definition of a current density operator, $\hat{\boldsymbol{j}}(\mathbf{r})$. The procedure is familiar from elementary textbooks on quantum mechanics. The second derivative reads

$$\ddot{n}(\mathbf{r}t) = \left(\frac{1}{i\hbar}\right)^2 \langle\Psi(t)\left|\left[[\hat{n}(\mathbf{r}),\hat{T}],\hat{H}(t)\right]\right|\Psi(t)\rangle \tag{1.31}$$

where $\hat{H}(t)$ is the Hamiltonian driving the time evolution in Eq. (1.28). This equation is readily recast into the shape

$$\delta\ddot{n}(\mathbf{r}t) = -\int d\mathbf{r}'\,\Xi(\mathbf{r}t,\mathbf{r}'t)\partial_{\mathbf{r}'}\phi_{\mathrm{ex}}(\mathbf{r}'t) \tag{1.32}$$

where we have introduced a correlator,

$$\Xi(\mathbf{r}t,\mathbf{r}'t) = \frac{i}{\hbar}\langle\Psi(t)\left|\left[\hat{\boldsymbol{j}}(\mathbf{r}'),\hat{n}(\mathbf{r})\right]\right|\Psi(t)\rangle \tag{1.33}$$

and the abbreviation

$$\delta\ddot{n}(\mathbf{r}t) = \ddot{n}(\mathbf{r}t) + \frac{1}{i\hbar}\partial_{\mathbf{r}}\langle\Psi(t)\left|\left[\hat{\boldsymbol{j}}(\mathbf{r}),\hat{T}+\hat{U}+\hat{V}_{\mathrm{ex}}\right]\right|\Psi(t)\rangle \tag{1.34}$$

The second term appearing in this expression describes the internal relaxation of the electron system ("gas" or "liquid"; e.g., due to viscoelastic forces).

The equal-time commutator in Eq. (1.33) is closely related to the density matrix; in terms of fermionic field operators, one has

$$n(\mathbf{r}t,\mathbf{r}'t) = \tfrac{1}{2}\langle\Psi(t)|\hat{\psi}^{\dagger}(\mathbf{r})\hat{\psi}(\mathbf{r}') + \hat{\psi}^{\dagger}(\mathbf{r}')\hat{\psi}(\mathbf{r})|\Psi(t)\rangle$$

so that

$$\Xi(\mathbf{r}t,\mathbf{r}'t) = \frac{1}{m}[n(\mathbf{r}t,\mathbf{r}'t)\partial_{\mathbf{r}'}\delta(\mathbf{r}-\mathbf{r}') - \delta(\mathbf{r}-\mathbf{r}')\partial_{\mathbf{r}'}n(\mathbf{r}t,\mathbf{r}'t)] \tag{1.35}$$

Feeding this expression back into Eq. (1.32) and recalling that $n(\mathbf{r}t,\mathbf{r}t)\equiv n(\mathbf{r}t)$, we recover Newton's third law,

$$\delta\ddot{n}(\mathbf{r}t) = \frac{1}{m}\partial_{\mathbf{r}}\,n(\mathbf{r}t)\partial_{\mathbf{r}}\phi_{\mathrm{ex}}(\mathbf{r}t) \tag{1.36}$$

as we should. Clearly, a spatially homogeneous part of the probing potentials can never be recovered from the density evolution, since such potentials do not

exert a force. By contrast, the inhomogeneous piece can be reconstructed from its accelerating effect on the density.[†] Technically speaking, Eq. (1.36) represents a linear, first-order (in space) differential equation for the probing field $\phi_{ex}(t)$. Combining with the Schrödinger equation (1.28),

$$i\hbar\partial_t\Psi(t) = \hat{H}(t)\Psi(t)$$

one obtains a system of two linear equations, which are local in time and readily integrated starting from the initial time $t = 0$.

This is how, in principle, the probing field may be reconstructed (up to a homogeneous constant), if only $n(\mathbf{r}t)$ is known: $n(\mathbf{r}t) \to \phi_{ex}(\mathbf{r}t)$. Since the other direction, $\phi_{ex}(\mathbf{r}t) \to n(\mathbf{r}t)$, is provided trivially by the Schrödinger equation, we readily conclude that

$$\phi_{ex}(\mathbf{r}t) \leftrightarrow n(\mathbf{r}t)$$

Extension   So far we have shown how the probing potential $\phi_{ex}(\mathbf{r}t)$ can be calculated if the density evolution and the initial state are given. It is also tacitly understood here that the Hamiltonian (i.e., the dispersion, $\hat{T}$, the electrostatic environment, $\hat{V}_{ex}$, and the interaction, $\hat{U}$) are known. Their structure cannot be reconstructed with $n(\mathbf{r}t)$.

In conjunction with Eq. (1.36), this last observation has an important implication. Consider, for example, two systems with two different interactions, $\hat{U}$ and $\hat{U}'$, and two different initial states, Ψ_i and Ψ_i', that both satisfy the condition that their initial density $n(\mathbf{r}t_i)$, together with the time derivative $\dot{n}(\mathbf{r}t_i)$, coincide. Under this condition, for both systems an equation of the type (1.36) holds true, since the derivation made no special assumption about the structure of $\hat{U}$. Therefore, for any (reasonable) interaction $\hat{U}$ we can find a time-dependent single-particle potential such that the density of the many-body system follows a predefined time evolution $n(\mathbf{r}t)$.

We can even go a step further. In fact, we have shown how to calculate $\hat{U}$-depending single-particle potentials, v_s, such that systems with different interactions can exhibit the same time-dependent density. This means, in particular, that we can model the time evolution $n(\mathbf{r}t)$ of interacting systems driven by $\phi_{ex}(\mathbf{r}t)$ by studying a reference system of noninteracting particles that experience a particular driving field $v_s(\mathbf{r}t)$. This field can be constructed from the (invertible) mapping

$$\phi_{ex}(\mathbf{r}t) \underset{\text{Eq. (1.28)}}{\overset{\hat{U}}{\leftrightarrow}} n(\mathbf{r}t) \underset{\text{Eq. (1.36)}}{\overset{\hat{U}'=0}{\leftrightarrow}} v_s(\mathbf{r}t) \tag{1.37}$$

at least in principle. Some of the conclusions, which we have arrived at here, were presented earlier by van Leeuwen[24] based on the same equations but with somewhat different arguments.[‡]

[†]This statement is true in those spatial regions where the particle density is nonvanishing $n(\mathbf{r}) \geq 0$.
[‡]We thank G. Stefanucci for bringing Ref. 24 to our attention and for a related discussion.

Remarks

- By including in addition to the scalar probing potential $\phi_{ex}(t)$ a vector probing potential, $A_{ex}(t)$, and keeping the current density explicit as a second collective field, one can generalize the argument presented above to derive a time-dependent current DFT. A proof in the spirit of van Leeuwen[24] has been given by Vignale.[25]

- Exactly the same arguments that have been presented for the case of a single wavefunction $\Psi(t)$ also apply to an ensemble of wavefunctions characterized by a statistical operator $\hat{\rho}$ with only minor modifications: (1) quantum mechanical expectation values turn into ensemble averages, and (2) the Schrödinger equation is replaced by the von Neumann equation

$$\dot{\hat{\rho}} = \frac{i}{\hbar}[\hat{\rho}, \hat{H}(t)] \tag{1.38}$$

  This prompts a generalization of TDDFT to finite temperatures.

- In principle, one can in this way also consider systems with a coupling to a heat bath (e.g., bosons). The only essential modification occurs in Newton's law, which now needs to account, for example, for a change in the effective dispersion $1/m$ due to the electron–boson coupling. First attempts to develop a TDDFT for a system coupled to reservoirs have been reported.[26–28]

- Notice that the appearance of the gradients in Eq. (1.36) is due to particle number conservation. The reason is that symmetric correlators of the type

$$\langle \Psi(t)|[[\hat{n}(\mathbf{r}), \hat{O}], \hat{n}(\mathbf{r}')]|\Psi(t)\rangle$$

  vanish after integration over one of the spatial coordinates if $\hat{O}$ commutes with the total particle number operator, $[\hat{O}, \hat{N}] = 0$. Indeed, in Eq. (1.31) this is the case, because any term in the Hamiltonian commutes with the total particle number operator $\hat{N}$. Hence, such correlators have vanishing (real space) Fourier components at zero wavenumbers, $\mathbf{q} = 0$. Assuming analyticity, we can say that the correlator is proportionate to the product of two wavenumbers, $\mathbf{q}$ and $\mathbf{q}'$, and for this reason two gradients appear in Eq. (1.36).

- The validity of time-dependent DFT is based on three elementary observations all of which relate to the fact that (quantum) mechanics is governed by linear differential equations in time:
  1. The total force can be deduced from its action on the particle density.
  2. This force can be split into an external and internal component; the internal component acting at time t can be calculated knowing just $\Psi(t)$.
  3. To calculate $\Psi(t)$, only forces acting prior to t and the initial conditions have to be known.

1.6.2 Dynamical Kohn–Sham Theory

The Runge–Gross theorem and its extensions teach us that there is a reference system of noninteracting particles living in a potential $v_s(\mathbf{r}t)$ [Eq. (1.37)], so that at $t > 0$ its density evolves in time in exactly the same way that it does for many-body system. The dynamics of this reference system are governed by an effective Schrödinger-type equation, the dynamic Kohn–Sham equations. With the decomposition $v_s = v_{\text{ex}} + v_{\text{H}} + v_{\text{XC}} + \phi_{\text{ex}}$, they read

$$\frac{i}{\hbar}\partial_t\phi_\ell(\mathbf{r}) = [\varepsilon(\hat{\boldsymbol{p}}) + v_{\text{ex}}(\mathbf{r}) + \phi_{\text{ex}}(\mathbf{r}t) + v_{\text{H}}(\mathbf{r}t) + v_{\text{XC}}(\mathbf{r}t)]\phi_\ell(\mathbf{r}) \qquad (1.39)$$

where $\phi_{\text{ex}}(\mathbf{r}t)$ is the time-dependent probing field and

$$n(\mathbf{r}, t) = \sum_{\ell=1}^{N} |\phi_\ell(\mathbf{r}t)|^2$$

$$v_{\text{H}}[n](\mathbf{r}t) = \int d\mathbf{r}' u(\mathbf{r} - \mathbf{r}')n(\mathbf{r}'t) \qquad (1.40)$$

The functional $v_{\text{XC}}[n](\mathbf{r}t)$ is the piece of $v_s[n](\mathbf{r}t)$ that accommodates the interactions beyond the mean field (Hartree) type. It depends on the time-dependent particle density, including its history. Moreover, as a first-order differential equation, Eq. (1.39) needs to be complemented with an initial condition. Part of this is, of course, that $n(\mathbf{r}, t = 0)$ coincides with the density of the many-body system at $t = 0$. However, in addition, the functional v_{XC} will in general also depend on the many-body wavefunction of the initial state, $\Psi_I \equiv \Psi(t = 0)$, which may—but does not have to be—an equilibrium state.

1.6.3 Linear Density Response

Consider a situation where the many-body system is in thermal equilibrium at times $t < 0$ before the probing field $\phi_{\text{ex}}(\mathbf{r}t)$ is switched on. Moreover, assume that the perturbation is going to be very weak, so that the requirements for the application of the linear response theory are met. Under this condition, an explicit expression for the XC-functional v_{XC} is readily written down.

Indeed, there is a matrix $\chi(\mathbf{r}t, \mathbf{r}'t')$, the density susceptibility, which relates the probing field to the (linear) system response, $\Delta n = n - n^{\text{eq}}$:

$$\Delta n(\mathbf{r}t) = \int dt' \int d\mathbf{r}' \, \chi(\mathbf{r}t, \mathbf{r}'t')\phi_{\text{ex}}(r't') \qquad (1.41)$$

The matrix $\chi(t, t')$ is an equilibrium correlation function of the system, and it therefore depends only on the time differences $t - t'$. We can use its inverse, χ^{-1}, to define an operator kernel f_{XC} via the decomposition

$$\chi^{-1} = \chi_{\text{KS}}^{-1} - f_{\text{H}} - f_{\text{XC}} \qquad (1.42)$$

The operator χ_{KS} describes the density response of the equilibrium KS system, ignoring the feedback of $\phi_{ex}(t)$ into v_H and v_{XC} [Eq. (1.39)]; explicitly,

$$\chi_{KS}(\mathbf{r}\mathbf{r}'z) = \frac{1}{\hbar} \sum_{\ell,\ell'} \langle \ell | \hat{n}(\mathbf{r}) | \ell' \rangle \langle \ell' | \hat{n}(\mathbf{r}') | \ell \rangle \frac{f(\varepsilon_\ell) - f(\varepsilon_{\ell'})}{\varepsilon_{\ell'} - \varepsilon_\ell - z}$$

where $|\ell\rangle$, $|\ell'\rangle$ and $\varepsilon_{\ell,\ell'}$ denote the unperturbed ($\phi_{ex} \equiv 0$) KS orbitals and KS energies and $z = \omega + i\eta$ lies in the complex plane. The feedback is then taken into account by $f_H = u(\mathbf{r} - \mathbf{r}')$ for the Hartree term v_H and by f_{XC} for the exchange correlation potential, v_{XC}, in Eq. (1.39).

From this point of view it is obvious how to construct the dynamic correction of the XC functional to the equilibrium functional:

$$v_{XC}[n](\mathbf{r}t) = v_{XC}^{eq}[n_{eq}](\mathbf{r}) + \int dt' \int d\mathbf{r}' f_{XC}(\mathbf{r}, \mathbf{r}'; t - t') \Delta n(\mathbf{r}'t') \qquad (1.43)$$

Remarks

- We have just constructed a single-particle theory, which has the property that it gives the correct linear dynamical response of the many-body system. The procedure relies on the familiar notions of linear response theory only and does not make reference to the underpinnings of the time-dependent DFT. It is emphasized here that the genuine statements of time-dependent DFT, when applied to systems that are in equilibrium at $t < 0$, reside in the claim that an effective single-particle description exists even outside the linear regime.

- Much of the recent improvement[29] in quantitative calculations of optical spectra of single molecules is due to including the terms f_H and in particular f_{XC} into the analysis (in addition to χ_{KS}), which have often been ignored before. In this way the single-particle spectrum of the bare Kohn–Sham system is dressed so as to produce the correct many-body excitations. Often, the success of this procedure is attributed to the time-dependent DFT. This is misleading, however, since it is merely the consequence of a proper application of the standard theory of linear responses.

- The best used approximation on f_{XC} is the adiabatic LDA (ALDA). It comprises two steps. First is the adiabatic approximation,

$$f_{XC}^{ad}(\mathbf{r}t, \mathbf{r}'t') = \left. \frac{\partial v_{XC}^{eq}[n](\mathbf{r}')}{\partial n(\mathbf{r})} \right|_{n(\mathbf{r}t)} \delta(t - t') \qquad (1.44)$$

This step, by definition, erases all memory effects, so a δ-function in time appears. The complete absence of memory suggests one more approximation, which also eliminates nonlocal correlations in space. This is necessary, because signal propagation occurs with a finite velocity and therefore always

has a retardation time. Therefore, density fluctuations in different spatial regions cannot be correlated instantaneously. This aspect is built into

$$f_{XC}^{ALDA}(\mathbf{r}t, \mathbf{r}'t') = \left.\frac{dv_{XC}^{eq}(n)}{dn}\right|_{n(\mathbf{r}t)} \delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \qquad (1.45)$$

automatically, where in Eq. (1.44) v_{XC}^{eq} has been replaced by its LDA approximant.

1.6.4 Time-Dependent Current DFT

The frequency structure of f_{XC} has been worked out in the hydrodynamic regime of small wavenumbers and frequencies by Kohn, Vignale, and co-workers.[30,31] It is seen explicitly there that severe memory effects indeed exist due to general conservation laws, which express themselves as singular behavior in correlation functions with respect to wavenumber and frequency.

As usual, singularities may be partly eliminated by reformulating in terms of correlation functions of the (generalized) velocities. In the case of the particle density, one introduces the longitudinal current density,

$$j^{\ell}(\mathbf{q}\omega) = \frac{-i\omega}{qn(\mathbf{q}\omega)} \qquad (1.46)$$

In this way one absorbs factors q^{-1}, thus removing nonlocal behavior in the density kernels, which indicates, for example, the slow density relaxation due to particle number conservation. In this spirit the time-dependent current DFT (TDCDFT) was developed.[30,31]

Apart from the fact that it works with current-density kernels, which are more local than those in TDDFT, TDCDFT offers yet another attraction. In addition to the density [or j^{ℓ}, Eq. (1.48)] it also features a second independent collective field, the transverse currents j^{t}. Therefore, TDCDFT can in principle also describe the orbital response to probing vector potentials (i.e., magnetic fields).

1.6.5 Appendix: Variational Principle

Unlike the case with equilibrium theory, a variational principle is not required in order to derive the dynamical Kohn–Sham equations. Still, it is desirable to have a formulation of TDDFT available in terms of an action, for example, because one may hope to be able to calculate v_s by performing a functional derivative. In this section we investigate the "naive" trial action

$$
\begin{aligned}
A[\tilde{\Psi}] &= \int_0^{\infty} dt \, \langle \tilde{\Psi}(t)| i\hbar\partial_t - \hat{H}(t) | \tilde{\Psi}(t) \rangle \\
&= \int_0^{\infty} dt \, \langle \tilde{\Psi}(t)| i\hbar\partial_t - \hat{T} - \hat{U} - \hat{V}_{ex} | \tilde{\Psi}(t) \rangle - \int_0^{\infty} dt \int d\mathbf{r}\phi_{ex}(\mathbf{r}t)\tilde{n}(\mathbf{r}t)
\end{aligned}
$$

$$(1.47)$$

which is defined over the space C_{Ψ_I} of complex fields $\tilde{\Psi}(t)$ with constraints given by (1) the antisymmetry requirement in all N coordinates $\mathbf{r}_1 \cdots \mathbf{r}_N$, and (2) the initial condition $\tilde{\Psi}(0) = \Psi_I$. The solution of the Schrödinger equation for a given external field $\phi_{ex}(\mathbf{r}t)$ is the one element $\Psi(t)$ of C_{Ψ_I} that optimizes $A[\tilde{\Psi}]$.

In full analogy to the equilibrium case, the functional equation (1.47) can be used as a basis to find an action functional of the density alone by preoptimizing. We first perform a decomposition of C_{Ψ_I} into subsets; the elements of each subset have the same evolution $\tilde{n}(\mathbf{r}t)$. Second, we find within each one of these subsets those states $\Psi_{\tilde{n}(\mathbf{r}t)}$ that are optimal with respect to $A[\tilde{\Psi}]$. These states form the ensemble M_{preopt} of preoptimized fields.[†]

In this way we arrive at an action functional, which is defined on M_{preopt}:

$$S_{\Psi_I}[\tilde{n}] = \int_0^\infty dt \, \langle \Psi_{\tilde{n}}(t) | i\hbar\partial_t - \hat{T} - \hat{U} | \Psi_{\tilde{n}}(t) \rangle \tag{1.48}$$

$S_{\Psi_{\tilde{n}}}$ is the dynamical analog of F [Eq. (1.37)]. The Schrödinger time evolution of the density, $n(\mathbf{r}t)$, is the single one that optimizes the full action,

$$A_{\Psi_I}[v_{ex}, \tilde{n}] = S_{\Psi_I}[\tilde{n}] - \int_0^\infty dt[v_{ex}(\mathbf{r}) + \phi_{ex}(\mathbf{r}t)]\tilde{n}(\mathbf{r}t) \tag{1.49}$$

The variational space associated with this action is spanned by all those $\tilde{n}(\mathbf{r}t)$ which are $\tilde{\Psi}$-*representable*: There is at least one element $\tilde{\Psi}(t)$ of C_{Ψ_I} such that $\tilde{n}(\mathbf{r}t) = \langle \tilde{\Psi}(t) | \hat{n}(\mathbf{r}) | \tilde{\Psi}(t) \rangle$.

Remarks

- Preoptimizing is a constrained minimum search in the subspace of possible wavefunctions that satisfy the initial condition (2). Therefore, each initial condition carries its own functional: $S_{\Psi_I}[n]$.
- By construction, the search over Ψ-representable densities leads to a variational equation,

$$\left. \frac{\delta S_{\Psi_I}[\tilde{n}]}{\delta \tilde{n}(\mathbf{r}t)} \right|_{\tilde{n}(\mathbf{r}t)=n(\mathbf{r}t)} = \phi_{ex}(\mathbf{r}t) + v_{ex}(\mathbf{r}) \tag{1.50}$$

Its solution, $n(\mathbf{r}t)$, defines the Schrödinger dynamics for the density corresponding to a given probing field $\phi_{ex}(\mathbf{r}t)$. A more explicit expression for the left-hand side may be obtained by taking the time derivative and comparing with Eq. (1.36).

[†]With every optimum $\Psi_{\tilde{n}}(t)$, the related function $e^{i\varphi(t)}\Psi_{\tilde{n}}(t)$ with $\varphi(0) = 0$ is an optimum, which differs by a time-dependent, spatially homogeneous phase shift. The shift merely reflects the necessity to fix the zero of energy. We identify all those states with one another that differ only by a spatially homogeneous phase $\varphi(t)$.

- Consider to generate all possible solutions of Eq. (1.50) by scanning through the space of all allowed (i.e., sufficiently smooth) probing fields $\phi_{ex}(\mathbf{r}t)$. This subset of the Ψ-representable variational space is called *v-representable*. An arbitrary element of the variational space $\tilde{n}(\mathbf{r}t)$ is certainly Ψ-representable but may not be v-representable.
- The Schrödinger dynamics is unitary: $N = \int d\mathbf{r}\, n(\mathbf{r}t)$ is an invariant of motion. v-representable states obey unitarity, but Ψ-representable states may not.
- By taking a functional derivative,

$$\frac{\partial}{\partial n(\mathbf{r}t)} \left. \frac{\delta S_{\Psi_I}[\tilde{n}]}{\delta \tilde{n}(\mathbf{r}'t')} \right|_{\tilde{n}=n} = \frac{\partial \phi_{ex}(\mathbf{r}'t')}{\partial n(\mathbf{r}t)} = \chi^{-1}(\mathbf{r}'\mathbf{r}, (t'-t)) \qquad (1.51)$$

a relation to the reciprocal of the density correlation function is derived. Note that the ∂ derivative relates to density differences within the set of all $n(\mathbf{r}t)$ that are v-representable. Our notation emphasizes this difference with the earlier δ derivative [Eq. (1.50)].

- The right-hand side of Eq. (1.51) is subject to causality; the density $n(\mathbf{r}t)$ indicates changes in the probing potential $\phi_{ex}(\mathbf{r}t')$ only at later times, $t > t'$. Equation (1.51) pays respect to this asymmetry, since the ∂ and δ derivatives must not be interchanged.
- The causality issue noted above makes it very obvious that an action principle should not be based solely on the variational space of v-representable histories $n(\mathbf{r}t)$. This issue has been discussed in detail by van Leeuwen.[23,32] In response, this author derives an action S employing the Keldysh formalism. The procedure by itself does appear to lead to fundamentally new insights. However, it has the charming feature against the naive starting point [Eq. (1.47)] that only one (enlarged) variational space for $n(\mathbf{r}t)$ appears. In addition, there is an important conceptual advantage, since—in principle—within this approach it is clear how one can calculate v_{XC} in a systematical perturbation theory.

1.7   TDDFT AND TRANSPORT CALCULATIONS

In this section we discuss the application of TDDFT in the context of charge transport. The focus will be on the dc limit. There are various ways how to formulate the transport problem; we shall elaborate on the consequences from linear response and scattering approaches. We concentrate on the presentation of those elementary facts that are specific of a treatment of transport within the framework of TDDFT. An attempt is being made to be as self-contained as possible.

1.7.1   Linear Current Response

One way to establish a current flow in a system, which initially is in a thermodynamic equilibrium, is to switch on an electric field $\mathbf{E}_{ex}(\mathbf{r}t)$. This field is not

the one that an electron feels when it accelerates. The accelerating (local) field, **E**, also contains an induced component,

$$\mathbf{E} = \mathbf{E}_{\text{ex}} + \mathbf{E}_{\text{ind}} \tag{1.52}$$

We restrict ourselves to initial situations that respect time-reversal invariance. Then the induced field is generated by a shift of charges, $e \, \Delta n$, under the influence of $\mathbf{E}_{\text{ex}}$; we have

$$\mathbf{E}_{\text{ind}}(\mathbf{r}t) = -\partial_{\mathbf{r}} \int d\mathbf{r}' u(\mathbf{r} - \mathbf{r}') \, \Delta n(\mathbf{r}'t) \tag{1.53}$$

By definition, the conductivity matrix, σ_{ij}, relates only the total field, **E**, to the linear response of the current density by

$$j_i(\mathbf{r}\omega) = \int d\mathbf{r}' \sigma_{ij}(\mathbf{r}, \mathbf{r}', \omega) E_j(\mathbf{r}'\omega) \tag{1.54}$$

To make contact to TDDFT, we decompose **j** into a longitudinal (curl free) piece, $\mathbf{j}^{\ell}$, and a transverse (source free) field, $\mathbf{j}^t$.

1.7.1.1 Magnetization (Transverse) Currents By construction, $\mathbf{j}^t$ incorporates the orbital ring currents that may be understood as a local magnetization density defined via $\mathbf{j}^t(\mathbf{r}t) = c\partial_{\mathbf{r}} \times \mathbf{m}(\mathbf{r}t)$, where c denotes the velocity of light. Non-vanishing magnetizations occur in equilibrium systems only in the presence of (spontaneously) broken time-reversal invariance. In these cases, the current DFT (CDFT) has to be employed, where the magnetization is explicitly kept as a second collective field in addition to the particle density. We consider here only systems that are invariant under time reversal. Then, ring currents vanish in the initial state, $\mathbf{j}^t = 0$. In such systems transverse currents can emerge in the presence of external driving fields.[†] Since they are not accompanied by density fluctuations, TDDFT does not monitor them. This implies, in particular, that the transverse currents of the time-dependent KS system do not, in general, coincide with the physical magnetization currents.

1.7.1.2 Longitudinal Currents The continuity equation connects $\mathbf{j}^{\ell}$ with the time dependency of the particle density. Therefore, the physical longitudinal current density and the longitudinal KS currents coincide. Hence, it makes sense to introduce a conductivity of the KS particles via

$$j_i(\mathbf{r}, \omega) = \int d\mathbf{r}' \sigma_{\text{KS},ij}(\mathbf{r}, \mathbf{r}', \omega)[E_{\text{ex}} + E_{\text{ind}} + E_{\text{XC}}]_j(\mathbf{r}', \omega) \tag{1.55}$$

[†]As an example we mention a ring current flowing in a perfectly conducting cylinder that closes around a time-dependent magnetic flux.

Just like physical particles, KS particles do not react to the external field but, rather, to the local field. This field contains the same Hartree-type term that originates from v_H in Eq. (1.39) and that was already present for the physical particles [Eq. (1.53)]. However, for KS particles not only v_H but also v_{XC} acquires a correction with a change in the density since

$$f_{XC}(\mathbf{r}, \mathbf{r}', t - t') = \frac{\partial v_{XC}[n](\mathbf{r}t)}{\partial n(\mathbf{r}'t')} \tag{1.56}$$

does not vanish [see Eq. (1.43)]. The resulting excess force $\mathbf{E}_{XC}$ from this contribution reads

$$\mathbf{E}_{XC}(r\omega) = -\partial_{\mathbf{r}} \int d\mathbf{r}' \, f_{XC}(\mathbf{r}, \mathbf{r}', \omega) \, \Delta n(\mathbf{r}', \omega) \tag{1.57}$$

in full analogy with Eq. (1.53).

Remark

- The exchange–correlation field $\mathbf{E}_{XC}$ comprises a piece that originates from the adiabatic term given in Eq. (1.44). On the level of the ALDA, we have

$$\mathbf{E}_{XC}^{ALDA}(\mathbf{r}\omega) = -\partial_{\mathbf{r}} \left. \frac{dv_{XC}^{eq}(n)}{dn} \right|_{n^{eq}(\mathbf{r})} \Delta n(\mathbf{r}, \omega) \tag{1.58}$$

  In addition, $\mathbf{E}_{XC}$ also comprises a second piece, which brings in the viscoelastic properties of the correlated electron liquid. This piece is usually ignored in TDDFT, because it is very difficult to formulate in a purely density-based language. This is not surprising, because the viscosity is intimately related to shear forces within the liquid that derive from mixed terms $\partial j_x/\partial y$ typical of transverse current patterns. Such forces are more naturally described within time-dependent current DFT.[30,31]

1.7.1.3   Quasi-One-Dimensional Wire   We consider as an illustrative example the dc response of a quasi-one-dimensional wire of length L to an electric field in longitudinal direction, $\mathbf{E}(\mathbf{r}) = e_z E(z)$. The dc current, I, is given by

$$I = \int_0^L dz' \, g_{KS}(z, z')[E_{ex} + E_{ind} + E_{XC}](z') \tag{1.59}$$

$$g_{KS}(z, z') = \iint d\mathbf{r}'_\perp \, d\mathbf{r}_\perp \, \sigma_{KS}(\mathbf{r}, \mathbf{r}') \tag{1.60}$$

where it was assumed that the longitudinal field components have negligible variation in the perpendicular wire direction $\mathbf{r}_\perp$. Since any configuration of driving fields has as an associated dc current I that is the same for all observation points

z, we conclude that the kernel (1.60) is independent of its arguments and define a KS conductance: $G_{KS} = g_{KS}(z, z')$.

$$I = G_{KS} \int_0^L dz' \, [E_{ex} + E_{ind} + E_{XC}](z') \tag{1.61}$$

The first two terms in the integral add up to the physical voltage drop, V, along the wire. The appearance of the third term indicates that the KS particles experience another voltage, which differs by the amount

$$V_{XC} = \int_0^L dz' \, E_{XC}(z') \tag{1.62}$$

Remarks

- The ALDA contribution to the effective driving field is conservative, so it may be written as a gradient of a potential,

$$\int_0^L dz' \, E_{XC}^{ALDA}(z') = -v_{XC}^{eq}(n(z))\big|_{n(0)}^{n(L)}$$

  As long as observation times are considered such that the effect of the charge transfer on the local charge density is still negligibly small (long wire limit), we can take $n(L) = n(0)$, so that the ALDA contribution vanishes (for macroscopically homogeneous wires). Nonzero contributions to V_{XC} come from the viscous term. The viscosity tends to reduce the response of the electron liquid to external forces. Density functional theories take this behavior into account by "renormalizing" the true forces with $\mathbf{E}_{XC}$.

- On a very qualitative level, the viscous forces tend to hinder the current flow through narrow constrictions with "sticky" walls. For this reason, their effect has been investigated in the context of current flows through single molecules.[33] However, as pointed out previously[19] (and what underlies the debate[34,35]), borrowing concepts from hydrodynamics to apply them on the molecular scale is not straightforward—for example, the viscosity: This describes how much momentum is transferred per time from a fast-moving stream to a neighboring one that flows into the same direction but with a lower speed. On a microscopic level, momentum exchange is mediated via collisions between the flowing particles. Therefore, it is clear that a description in terms of the macroscopic parameter "viscosity" can be valid only on length and time scales that substantially exceed the interparticle scattering length and time. Both scales become very large in fermion systems at low temperature, and in particular can easily exceed the dimensions of those atomistic or molecular systems that one would like to treat. Applications in mesoscopic semiconductors enjoy a much better justification.

1.7.2   Scattering Theory

The linear response theory is a framework for calculating the dynamical reaction to linear order in the probing field of any many-body system. Its advantage is that it is completely generally applicable. For the same reason, situations are easily identified, where alternative formalisms are better adapted and therefore allow a simpler and more transparent analysis.

In this section we consider an example thereof—the dc transport through a quantum dot (e.g., a molecule) which has been wired to a left and a right reservoir (see Fig. 1.4). We consider quasi-one-dimensional well-screened wires, so that particles inside the wire do not interact with each other. The traveling waves along the wire are categorized by *scattering states*. Each such state is equipped with a continuous longitudinal degree of freedom associated with a wavenumber, k, a discrete transverse degree, the *channel index n* [which should not be confused with the particle density $n(\mathbf{r})$], and a dispersion relation $E_n(k)$. In this language the current flowing through the wire is described by a superposition of scattering states.

How the particles that enter the wire from a reservoir distribute over the available scattering states is dictated by distribution functions, $f_{L,R}(E)$, which are properties solely of the left and right reservoirs. The specifics of the quantum dot enter the construction of the scattering states in terms of the reflection and transmission coefficients, $\tilde{r}_{nn'}(E, E')$ and $\tilde{t}_{nn'}(E, E')$. They describe the probability amplitude for a particle that approaches the quantum dot with energy E in channel n to be either reflected or transmitted into the channel n' with energy E'.

1.7.2.1   Landauer Theory   The scattering description is particularly convenient if scattering is elastic, so in each single scattering process the state of the quantum dot is preserved; in particular, each scattering event conserves the energy of the incoming particle, $E = E'$. Under this specific condition, the current is simply given by the Landauer formula,

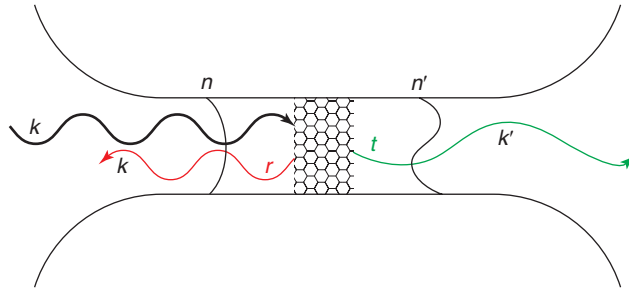$$I = \int dE \, T(E)[f_L(E) - f_R(E)] \tag{1.63}$$

Fig. 1.4 (color online)   Wiring a molecule to source and drain reservoirs: scattering states description with longitudinal (k) and transverse (n) quantum numbers.

with a transmission function

$$T(E) = \sum_{nn'} |t_{n'n}(E)|^2 \equiv \mathrm{Tr}\, tt^\dagger \tag{1.64}$$

where $t_{n'n} = \tilde{t}_{\nu'\nu}(v_\nu/v_{\nu'})^{1/2}$, with $v_\nu = \partial \varepsilon_\nu(k)/\partial k$ being the group velocity of particles traveling in channel n with energy E. Here we follow the common convention that each reservoir acts as a thermal bath characterized by a temperature and an electrochemical potential, $\mu_{L,R}$. Then the distributions $f_{L,R}$ are simply Fermi functions with bath parameters.

1.7.2.2 *Scattering Theory and TDDFT: Relaxation Problem*   Scattering theory describes a nonequilibrium situation that is (quasi-)stationary in time. Even though a current flows, expectation values of local (intensive) operators, in particular of $\hat{j}(\mathbf{r})$ and $\hat{n}(\mathbf{r})$, are time independent.[†] By contrast, TDDFT has been developed to describe the time evolution of the density, $n(\mathbf{r}t)$, under the action of a time-dependent potential, $\phi_{ex}(t)$, away from some initial condition. Both approaches may apply simultaneously if in the course of time evolution a quasistationary nonequilibrium situation develops.[36–38]

This can happen if the superposition of $\phi_{ex}(t)$ and the induced field, $v_{ind}(t)$, shifts the electrochemical potentials of the two reservoirs against each other:

$$[v_{ex}(\mathbf{r}t) + v_{ind}(\mathbf{r}t)]_L^R \underset{t \gg \tau_{trans}}{\to} \mu_R - \mu_L \tag{1.65}$$

Then, after waiting a time τ_{trans} in which transient dynamic phenomena have died out due to internal relaxation processes, a flow may establish that indeed it is quasistationary. The current will be monitored properly by TDDFT, since it equals the flux of particles out of one of the reservoirs: $I = \dot{N}_L = -\dot{N}_R$.

In this quasistationary regime, by definition the particle and current densities are time independent. One might then suspect that the KS potentials should also have become stationary. This point is perhaps not quite as obvious as it might look. Namely, the fact that the density is time independent by itself does not always imply that the Hamiltonian is stationary. For example, homogeneous ring systems that close around time-dependent fluxes can exhibit time-dependent ring currents that leave the density completely invariant. To exclude such artifacts, one can operate with probing fields $\phi_{ex}(t)$ that couple to the density itself and that become time independent after switching on. Then, at least in the linear response regime, functionals are guaranteed to become time independent, since they derive from linear-response kernels [Eq. (1.43)] (see the remark below).

Once we accept that potentials become stationary, we may define scattering states. However, whether this concept is useful or not depends on whether one

---

[†]We are assuming here that the reservoirs are ideal. They remain in thermodynamic equilibrium with fixed temperature, chemical potential, and so on, even in the presence of a current flow. In reality, this condition requires a separation of scales: macroscopic reservoirs and microscopic currents.

can identify the rules pertaining to how the physical current should be constructed from them. Whether or not the same rules apply for the KS scattering states of TDDFT that work for the truly noninteracting case is not a priori clear, however.

Indeed, after switching on the bias voltage, V, the workfunction of each reservoir shifts against the vacuum level. Apart from this effect, each reservoir stays in complete thermal equilibrium due to their macroscopic size each all the time. According to the general principles of the DFT outlines in earlier sections, the distribution function of KS particles inside each reservoir should still be given by $f_{L,R}$ with the appropriate chemical potentials $\mu_{L,R}$ and $eV = \mu_L - \mu_R$, as usual. This was the point of view that has been adopted elsewhere.[36]

However, this conclusion is not fully consistent with a result that we derived above. Namely, as we have seen in the linear response theory, the KS voltage does *not* in general coincide with the difference of the reservoir workfunctions. This effect has been incorporated[37,38] using Fermi functions with chemical potentials that do not coincide with physical values. Here it remains an open question as to how this finding could be reconciled with the requirement that each reservoir must stay in its own equilibrium. This apparent inconsistency of DFT-based scattering theory at the moment is seemingly unresolved.

Remarks

- The precise conditions under which a nonequilibrium current flows in a quasistationary manner are very difficult to state. That flow at small enough currents is always quasistationary is supported by linear response analysis. It suggests (1) that linear responses to a sufficiently weak field never mix frequencies (i.e., they simply follow the external stimulus in time). Furthermore, (2) slow-enough driving fields, $\omega\tau_{trans} \ll 1$, signalize the dc behavior. So, combining (1) and (2), one concludes that the linear regime should always be quasistationary.

- A breakdown of the quasistationary regime at sufficiently large currents is suggested by analogy to hydrodynamics as described by the Navier–Stokes equations. Here it is known that a laminar (i.e., quasistationary) regime should be separated from turbulence that develops at larger currents. Since at least on a qualitative level, the micro- or nanoscopic flow of the electron liquid is also a hydrodynamic phenomenon, a "turbulent" regime could exist here as well. This is also supported from the observation that the TDDFT equations are nonlinear in the density and therefore should host chaotic regimes.

1.8 MODELING RESERVOIRS IN AND OUT OF EQUILIBRIUM

1.8.1 External and Internal Hilbert Spaces

Scattering theory operates in a basis of scattering states; that is, it uses those quantum numbers that reflect the behavior of wavefunctions in the asymptotic (i.e., free of scattering potential) region of space (the *external Hilbert space*).
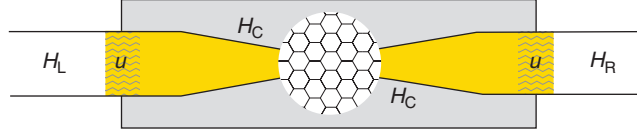
Fig. 1.5 (color online)   Partitioning of the scattering zone near a molecule or quantum dot underlying the Hamiltonian equation (1.66).

For some applications, this representation is suboptimal. From a computational perspective, this can happen if the Hilbert space of states in the vicinity of the scatterer (the *internal* or *microscopic Hilbert space*) is very large or complicated, so that computations do not allow us to keep explicit track of additional degrees of freedom. For example, if one is to describe the current flow through a molecule (molecular electronics)or a quantum dot, one can keep molecular states that incorporate the molecule itself plus the states of a few lead atoms. The entire contact, which encompasses 10^{23} atoms, can certainly not be dealt with in a computer.

   In more technical terms, we consider a partitioning of the system into left and right asymptotic regions, which are connected by a center region as given in Fig. 1.5 and detailed in the Hamiltonian

$$H = \begin{pmatrix} H_L & u^\dagger & 0 \\ u & H_C & v \\ 0 & v^\dagger & H_R \end{pmatrix} \tag{1.66}$$

The matrices $H_{L,R}$ comprise all the leads and are macroscopic, whereas H_C describes only the scattering region and therefore should have a microscopic size. If H_C is still very complicated, a formulation is desired that does not refer explicitly to the external, macroscopic Hilbert space (leads and reservoirs) but just focuses on the internal space. Roughly speaking, one would like to convert the trace over the external, channel degrees of freedom [Eq. 1.64] into another trace, which is only over the internal space of the molecule or quantum dot.

   A formal way to derive such a representation employs the *Keldysh technique*, also referred to as the *nonequilibrium Green's function method*.[39] For noninteracting particles it yields predictions for physical observables which are identical to the scattering theory. Similar to earlier authors,[40] we employ the latter method here to derive the key formulas that underlie a great many applications of ab initio transport calculations for nanostructures.

1.8.2   Born Approximation, $\hat{T}$-Matrix, and Transmission Function

Consider the situation where the left and the right leads are decoupled, $u = v = 0$ at $t = 0$. As before, we denote their eigenstates by a pair of indices $|nk\rangle$ (left) and $|n'k'\rangle$ (right). When contact is established at $t = 0$, an initial state $|nk\rangle$ becomes unstable. It can decay into the state $|n'k'\rangle$. The rate for this process is given

to lowest order by the Born approximation, which is equivalent to the familiar "golden rule" when applied to the scattering problem:

$$\hbar\tau_{n'n}^{-1}(E_n(k)) = 2\pi\delta(E_n(k) - E_{n'}(k'))|\langle n'k'|\hat{T}(E_n(k)|nk\rangle|^2 \tag{1.67}$$

Here, we have already refined the bare expression by introducing the $\hat{T}$-matrix, which makes it formally exact. How to relate $\hat{T}$ to the original Hamiltonian, (1.66), will be shown in Section 1.8.3.

The right-going current injected in this way from a left-hand-side wire state $|nk\rangle$ into the right lead is just

$$\sum_{n'}\int dk'\, \tau_{n'n}^{-1}(E_n(k))f_L(E_n(k))(1 - f_R(E_{n'}(k')))$$

where $f_L(E_n(k))$ is the occupation of the initial state and $1 - f_R(E_{n'}(k'))$ is a measure of the available space in the final state. The total current is the difference between all right- and left-flowing components:

$$I = e\sum_{n'n}\int dk\, dk' \tau_{n'n}^{-1}(E_n(k))[f_L(E_n(k)) - f_R(E_{n'}(k'))] \tag{1.68}$$

Comparing this expression with the Landauer formula, Eq. (1.63), we conclude that

$$T(E) = \sum_{n'n}\int dk\, dk'\, \delta(E - E_n(k))\tau_{n'n}^{-1}(E) \tag{1.69}$$

$$= (2\pi)^2 \sum_{n'n}\int dk\, dk'\, \delta(E - E_n(k))\delta(E - E_{n'}(k'))|\langle n'k'|\hat{T}(E)|nk\rangle|^2 \tag{1.70}$$

$$= \sum_{n'n}\frac{(2\pi)^2}{|v_n v_{n'}|}|\langle n'k'|\hat{T}(E)|nk\rangle|^2 \tag{1.71}$$

where the last line should be complemented with $E = E_n(k) = E_{n'}(k')$. Keeping Eq. (1.64) in mind, we have the identification (up to a phase factor)

$$t_{n'n} = \frac{2\pi}{\sqrt{|v_n v_{n'}|}}\langle n'k'|\hat{T}(E)|nk\rangle \tag{1.72}$$

Equation (1.70) has a compact notation if one introduces separate traces $\mathrm{Tr}_{L,R,C}$ over the Hilbert spaces of $H_{L,R,C}$:

$$T(E) = (2\pi)^2 \mathrm{Tr}_R[\delta(E - H_R)\hat{T}(E)\delta(E - H_L)\hat{T}^{\dagger}(E)] \tag{1.73}$$

1.8.3 $\hat{T}$-Matrix and Resolvent Operator

We now specify how to relate $\hat{T}$ to the original Hamiltonian, H, detailed in Eq. (1.66). Our derivation starts with the observation that all information about transport across the center region is encoded in the *resolvent operator*,

$$G(z) = \frac{1}{z - H} \tag{1.74}$$

Retarded (advanced) operators are defined via $G^{\text{ret}}(E) = G(E + i\eta)[G^{\text{av}}(E) = G(E - i\eta)]$; the matrix elements $\langle \mathbf{x}|G^{\text{ret,av}}(E)|\mathbf{x}'\rangle$ define the Green's functions.[†]

Actually, we care only for transfer processes, so only those matrix elements $\langle n'k'|G(z)|nk\rangle$ are of interest that connect states in the left and right leads. The corresponding off-diagonal sector of the full resolvent matrix may be obtained from an elementary matrix inversion. Its matrix elements have the property

$$\langle n'k'|G(z)|nk\rangle = \langle n'k'|g_{\text{R}}(z)[v^{\dagger}G_{\text{C}}(z)u]g_{\text{L}}(z)|nk\rangle \tag{1.75}$$

The matrix product that appears here inside $\langle \cdots \rangle$ has the form familiar from the Dyson equation in T-matrix notation[41]:

$$G = G_0 + G_0\hat{T}G_0 \tag{1.76}$$

where $G_0^{-1} = z - H_0$ is the bare Green's function in the absence of an interlead coupling, $u, v = 0$. In Eq. (1.75) the first term in the Dyson equation is missing, since the off-diagonal matrix elements that connect different leads vanish if there is no transmission.

Thus it is clear that the desired relation is just

$$\hat{T}(z) = v^{\dagger}G_{\text{C}}(z)u \tag{1.77}$$

with the resolvent operators of the central region and the leads

$$G_{\text{C}}(z) = \frac{1}{z - H_{\text{C}} - \Sigma_{\text{R}} - \Sigma_{\text{L}}} \tag{1.78}$$

$$g_{\text{R,L}}(z) = \frac{1}{z - H_{\text{R,L}}} \tag{1.79}$$

and self-energies

$$\Sigma_{\text{L}}(z) = ug_{\text{L}}(z)u^{\dagger} \qquad \Sigma_{\text{R}}(z) = vg_{\text{R}}(z)v^{\dagger} \tag{1.80}$$

[†]The infinitesimal parameter η in Eq. (1.74) shifts the poles of G into the complex plane. In this way it is ensured that the density of states, $-(1/\pi)\Im G(E + i\eta)$, becomes a smooth function of energy. Otherwise, the Hamiltonian (1.66) could not model metallic reservoirs, which by definition have a smooth, nonvanishing density of states near the Fermi energy.

Notice that G and $\Sigma_{R,L}$ act on the Hilbert space of H_C only, whereas $g_{R,L}$ acts on the spaces of $H_{R,L}$.

With this result, we can rewrite Eq. (1.73),

$$T(E) = \text{Tr}_C[\Gamma_L G_C^{\text{ret}}(E) \Gamma_R G_C^{\text{av}}(E)] \tag{1.81}$$

where we have introduced

$$\Gamma_L = 2\pi u \delta(E - H_L) u^\dagger \qquad \Gamma_R = 2\pi v \delta(E - H_R) v^\dagger \tag{1.82}$$

so that $\Gamma_{R,L} = -2\Im\Sigma_{R,L}^{\text{ret}}.^\dagger$ Equation (1.81) is the desired relation. The leads appear only implicitly in the self-energies, $\Sigma_{L,R}$; they have been "integrated out."

Remarks

- Formula (1.81) is most useful whenever (1) one can give recursive algorithms, so Σ can be calculated without having to deal with the full Hilbert space at a time, or (2) one can design approximations for Σ so that it is not necessary to deal with the Hilbert space of the leads at all. One can argue that simple but highly accurate approximations can indeed be given if H_C is "large enough", (i.e., comprises a sufficiently large part of the leads).

- Almost all scientific works that perform a *channel decomposition* begin by rewriting Eq. (1.81), which employs the matrix

$$\tau = \Gamma_L^{1/2} G_C \Gamma_R^{1/2} \tag{1.83}$$

so that by construction, $T(E) = \text{Tr}_C \tau \tau^\dagger$. Authors interpret τ as a transmission matrix and hence identify the eigenvectors of $\tau \tau^\dagger$ as the transmission channels. We wish to point out here that this widespread practice has to be taken with a grain of salt.

1. The trace in Eq. (1.81) is over the states of the central region and *not* over the (transverse) Hilbert space of the leads. Ironically, this is why we have derived it in the first place. Therefore, the matrix product in $\text{Tr}_C[\cdots]$ acts on a Hilbert space that is disconnected from the transverse lead space, where the product $tt^\dagger$ that appears in the Landauer formula, Eq. (1.63), lives. Hence, the channels of the leads and the eigenvectors of $\tau \tau^\dagger$ have nothing to do with each other.

2. In particular, τ should not be confused with the true transfer matrix t, given in Eq. (1.72).

3. One of the irritating artifacts that an uncontemplated adoption of this practice may prompt is related to the fact that the size of the central Hilbert space is a matter of convention. For this reason, the common channel analysis produces results that cannot be, in general, model

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†We have used $\delta(E) = (i/2\pi)[G(E + i\eta) - G(E - i\eta)]$.

independent. For example, the number of transmitting states (evanescent and propagating ones) may increase with the Hilbert space size. A more detailed discussion of this and related issues can be found elsewhere.[42,43]

1.8.4 Nonequilibrium Density Matrix

So far, we have used scattering theory to describe the current flow through a nanojunction or molecule. A very similar analysis allows us to derive even a slightly more general object, the density matrix, $\rho(\mathbf{x}, \mathbf{x}')$, in the presence of nonequilibrium. It is a matrix representation of the operator

$$\hat{\rho} = \sum_n \int dk \, |nk\rangle^{\mathrm{r}} {}^{\mathrm{r}}\langle nk| f_L(E_n(k)) + \sum_{n'} \int dk' \, |n'k'\rangle^{\mathrm{l}} {}^{\mathrm{l}}\langle n'k'| f_R(E_{n'}(k')) \quad (1.84)$$

where $|nk\rangle^{\mathrm{r}}$ ($|n'k'\rangle^{\mathrm{l}}$) denote the right (left)-going states emerging from the left (right) electrodes. The diagonal elements are of particular importance, since they give the particle density, $n(\mathbf{x}) = \rho(\mathbf{x}, \mathbf{x})$, at any position $\mathbf{x}$:

$$\rho(\mathbf{x}, \mathbf{x}) = \sum_n \int dk \, |\langle \mathbf{x}|nk\rangle^{\mathrm{r}}|^2 f_L(E_n(k))$$

$$+ \sum_{n'} \int dk' \, |\langle \mathbf{x}|n'k'\rangle^{\mathrm{l}}|^2 f_R(E_{n'}(k')) \quad (1.85)$$

In this section we repeat what we did in the previous section for the Landauer formula, but now for the density matrix. We derive an expression that relates those elements of $\hat{\rho}$ from the central Hilbert space only, in terms of G_C and $\Sigma_{\mathrm{L,R}}$ alone.

Indeed, consider the expression for the equilibrium density per spin inside the central region:

$$n^{\mathrm{eq}}(\mathbf{x}) = \int dE \, \langle \mathbf{x}|\delta(E - H)|\mathbf{x}\rangle f^{\mathrm{eq}}(E) \quad (1.86)$$

Employing a series of standard transformations, which rely upon nothing but the definitions given in the preceding section, we may cast it into a form that is already similar to Eq. (1.85):

$$n^{\mathrm{eq}}(\mathbf{x}) = -\frac{1}{2i\pi} \int dE \, \langle \mathbf{x}|G_C^{\mathrm{ret}}(E) - G_C^{\mathrm{av}}(E)|\mathbf{x}\rangle f^{\mathrm{eq}}(E) \quad (1.87)$$

$$= -\frac{1}{\pi} \int dE \, \langle \mathbf{x}|G_C^{\mathrm{ret}}(E) \left[\Im\Sigma_{\mathrm{L}}^{\mathrm{ret}} + \Im\Sigma_{\mathrm{R}}^{\mathrm{ret}}\right] G_C^{\mathrm{av}}(E)|\mathbf{x}\rangle f^{\mathrm{eq}}(E) \quad (1.88)$$

$$= \frac{1}{2\pi} \int dE \, \langle \mathbf{x}|G_C^{\mathrm{ret}}(E) \left[\Gamma_{\mathrm{L}} + \Gamma_{\mathrm{R}}\right] G_C^{\mathrm{av}}(E)|\mathbf{x}\rangle f^{\mathrm{eq}}(E) \quad (1.89)$$

$$= \sum_n \int dk \, |\langle \mathbf{x}|G_C^{\mathrm{ret}}(E_n(k))u|nk\rangle|^2 f^{\mathrm{eq}}(E_n(k))$$

$$+ \sum_{n'} \int dk' \, |\langle \mathbf{x}|G_C^{\mathrm{ret}}(E_{n'}(k'))v|n'k'\rangle|^2 f^{\mathrm{eq}}(E_{n'}(k')) \qquad (1.90)$$

The states $|nk\rangle$ ($|n'k'\rangle$) denote the eigenstates of the left (right) lead in the absence of a coupling, $u, v = 0$. Comparing Eq. (1.90) with the equilibrium limit of Eq. (1.85), $f^{\mathrm{eq}} = f_L = f_R$, suggests the identification

$$\langle \mathbf{x}|nk\rangle^r = \langle \mathbf{x}|G_C^{\mathrm{ret}}(E_n(k))u|nk\rangle \qquad (1.91)$$

$$\langle \mathbf{x}|n'k'\rangle^l = \langle \mathbf{x}|G_C^{\mathrm{ret}}(E_{n'}(k'))v|n'k'\rangle \qquad (1.92)$$

for point $\mathbf{x}$ inside the central region. The educated reader may recognize the relations above as an incarnation of the well-known Lippmann–Schwinger equation. Thus equipped, we rephrase the original expression for the density operator in the following way:

$$\hat{\rho} = \int \frac{dE}{2\pi} [G_C^{\mathrm{ret}} \Gamma_L G_C^{\mathrm{av}} f_L(E) + G_C^{\mathrm{ret}} \Gamma_R G_C^{\mathrm{av}} f_R(E)] \qquad (1.93)$$

which is valid inside the central region (matrix notation suppresses the argument energy, E). This equation is the main result of the present section. Needless to say, by differentiating off-diagonal elements of $\hat{\rho}$, the current density and therefore also the Landauer formula may be rederived.

1.8.5   Comment on Applications

By far the largest fraction of the vast body of DFT-based transport literature employs scattering theory in the formulation of the preceding section. The logic is that one solves the KS equations (1.39) with a particle density, $n(\mathbf{x})$, which is calculated from the nonequilibrium density operator (1.93), which also takes the reservoirs into account. The KS-Hamiltonian is then used, in turn, to construct the central Green's function and finally, also, the transmission function, (1.81), and the current, (1.63). In this final section we comment briefly on several general aspects of this research. Also, practical aspects of applications in spintronics and molecular electronics are highlighted in Chapters 18 and 19, respectively.

Transmission functions, $T(E)$, are of interest mostly near the Fermi energy, E_F, since one has for the zero-bias conductance, $G = T(E_F)$. In this region, $T(E)$ usually is dominated by the resonances originating from just two (transport) frontier orbitals. Calculations should yield the positions $E_{\mathrm{Ho, Lu}}$ and the broadenings $\Gamma_{\mathrm{Ho, Lu}}$ of the resonances.

In the case of resonances that do not interfere with others (*isolated resonances*), these parameters may be extracted by simply fitting a Breit–Wigner (Lorentzian) lineshape to $T(E)$. Sometimes more complicated situations exist,

where electrons can flow through the molecule via different paths that interfere with each other.[44] In this case the lineshape is not just a Lorentzian, but may, for example, be of the Fano type. Also, this structure is characterized by very few parameters only, which may be extracted from a suitable fit.

The numerical accuracy of both types of parameters, resonance positions and line widths, that one can get from the DFT-transport calculation depends on the approximations made in the underlying exchange correlation (XC) functional, of course. In transport calculations additional complications arise due to the presence of the electrodes (or reservoirs), which make it necessary to find a good approximation for the self-energies $\Sigma_{R,L}$.

1.8.5.1   Self-Energies $\Sigma_{R,L}$ The self-energies are crucial for the calculation of the resonance width. This is obvious, since without them, $\Sigma_{R,L} = 0$, there would be no level broadening at all: Each transport resonance would be arbitrarily sharp. Therefore, care is needed with the construction of these objects.

However, quite in contrast to a widespread perception in the scientific community, it is *not* necessary—and in practice not even always helpful—to perform an exact construction of $\Sigma_{R,L}$ along the lines of Eq. (1.80). This point has been made earlier[19,45,46] and we rephrase it here.

Consider the KS equation of the central region in the presence of a coupling to the electrodes:

$$[E - H_C - \Sigma_L(E) - \Sigma_R(E)]|\Psi\rangle = 0 \qquad (1.94)$$

The Hermitian sector of Σ adds to the Hamiltonian H_C and therefore shifts the bare eigenvalues of H_C. The anti-Hermitian sector, $\Gamma_{L,R}$, leads to a violation of the continuity equation; it shifts eigenvalues away from the real axis into the complex plane, thus providing a finite lifetime.

The physics that is incorporated in this way is transparent: Any traveling wave that moves toward the interface between the central region and the left and right electrodes will just penetrate it without being backscattered. From the viewpoint of the central system, the interface is absorbing. It is well known since the early days of nuclear physics that proper modeling of absorbing boundaries is via optical (i.e., non-Hermitian) potentials. This is exactly what the self-energy does.

With this picture in mind, it is obvious that an interface modeling of $\Gamma_{L,R}$ with the property that incident waves are fully absorbed will give the same values for positions and lifetimes of transport resonances. Therefore, as long as the boundary of the central region does not itself hinder the current flow, a modeling of Γ in terms of an optical potential will give accurate results. All the material specifics that are contained in the exact $\Gamma_{L,R}$ matrices can readily be ignored. To meet the condition for simple modeling, in practical terms the central region should comprise pieces of the electrodes that are large enough. Then complete absorption may be achieved with a leakage rate per interface site η that is still sufficiently small, to prevent feedback into the resonance energies.

1.8.5.2 System-Size Dependency: Separation of Scales To the best of our knowledge, all prominent DFT-based transport codes work with approximated self-energies. Unfortunately, a systematic check of quantitative results on the approximation scheme used is still not a standard procedure. If optical potentials with strength η are employed, the transmission resonances, Γ, that we would ultimately like to calculate should be invariant under a change of η by a factor of 10 or more.

The existence of such an invariance is a consequence of a separation of scales. The transport resonances reflect the lifetime of a state located in that subregion ("bottleneck") of the central region, which determines the resistance (see Fig. 1.5). If the particle has escaped this region, it vanishes into the leads once and for all—in reality. To catch this aspect, the modeling parameter η has just to be big enough to prevent the model particle from returning to the bottleneck. If the size of the central region is taken sufficiently large, much larger than the bottleneck, one can allow for $\eta \ll \Gamma$, and a separation of scales has been achieved.

Remark

- Self-energies, Σ, offer a rich toolbox for including effects of reservoirs with precision without keeping a large number of degrees of freedom explicit in the calculations. Recent applications of the principle describe systems with an inhomogeneous magnetization.[47] Also in this context, working with model self-energies rather than (formally) exact expressions proves reasonably accurate and highly useful.[48]

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