OSCILLATOR STRENGTHS FROM TIME-DEPENDENT DENSITY FUNCTIONAL THEORY

BY HEIKO APPEL

A thesis submitted to the

Graduate School—New Brunswick

Rutgers, The State University of New Jersey

in partial fulfillment of the requirements

for the degree of

Master of Science

Graduate Program in Physics and Astronomy

Written under the direction of

Kieron Burke

and approved by

_____

_____

_____

New Brunswick, New Jersey

October, 1999

ABSTRACT OF THE THESIS

OSCILLATOR STRENGTHS FROM TIME-DEPENDENT DENSITY FUNCTIONAL THEORY

by Heiko Appel

Thesis Director: Kieron Burke

We consider different forms of single-pole approximations (SPA) for oscillator-strengths in the response formalism of time-dependent density functional theory. Numerical calculations of oscillator strengths are presented for a simple model system, Hooke's atom, and various ions of the Helium isoelectronic series with charges Z=2,4,10,20,80. Starting with the Kohn-Sham Hamiltonian as an unperturbed system the oscillator strengths are treated in first order Görling-Levy perturbation theory. It is then proven that the first order correction for the oscillator strengths vanishes for harmonic external potentials.

Table of Contents

List of Tables

Chapter 1

Introduction

Density Functional Theory is a general approach for the calculation of properties of interacting many electron systems such as atoms, molecules or solids. It has become very popular in chemistry in the last decade due to the development of accurate functionals. The original scheme as proposed by Hohenberg and Kohn [1] and Kohn and Sham [2] is a ground-state theory which provides a reliable and inexpensive method for the calculation of the ground-state energy of an interacting many electron system. As a function of external parameters, the electronic ground-state energy can be used to extract a wealth of observable quantities, such as bond lengths and angles in the case of molecules, electric dipole moments, electric quadrupole moments, static polarizabilities, infrared intensities, magnetic susceptibilities, Raman intensities, etc.

Although the rigorous legitimization and therefore origin of the theory has to be traced back to the proof of the Hohenberg Kohn theorem and the formulation of the Kohn-Sham equations some 30 years ago, the ideas contained in the density functional approach to the many-body problem have been influenced by different historical developments.

One of these is concerned with the notion of an effective one-particle Hamiltonian and the issue of self-consistency. In 1928 Hartree [3] suggested an approximation to the N-particle Hamiltonian which was aimed at the construction of an effective single particle Hamiltonian. In this approximation every electron is assumed to move in an effective potential composed of the external potential caused by the nuclei and a contribution which describes the average electrostatic repulsion between the electrons. The total approximate Hamiltonian is then the sum of the effective one particle Hamiltonians, and the approximate wavefunction can be written as product of one particle orbitals which are the solution of the corresponding one particle Schrödinger equation. This approximation had, however, the problem that it ignored the antisymmetry of the total wavefunction and that the effective one-particle potential was not self-interaction free,

i.e., the electron whose effective potential has to be determined contributes via the total charge density already to its own effective potential therefore causing a self-interaction error.

The antisymmetry problem was circumvented in 1930 by Fock [4] who suggested using an already antisymmetric Slater determinant as a trial function for the Rayleigh-Ritz variational principle. Assuming again, as an approximation for the N-particle Hamiltonian, a sum of effective one-particle Hamiltonians leads then via the variational principle to the Hartree-Fock equations [5, 6, 7]. The requirement of antisymmetry leads in addition to the classical Hartree term in the effective one-particle potential to a so called exchange term. This contribution to the effective potential has no classical counterpart. It depends beside the eigenstate which is considered on all other eigenstates of the effective Hamiltonian and is a fully nonlocal contribution. The corresponding one particle Schrödinger equation is a multidimensional integro-differential equation which is in addition also nonlinear. The practical solution of these equations is done in a self-consistent manner. One starts with a guess for the effective potential, solves then the Hartree-Fock equations for the new one particle orbitals and constructs from those a new effective potential. This cycle is iterated until self-consistency is reached. The ideas of an effective one-particle Hamiltonian and a self-consistent solution originating from these historical developments were later incorporated in the Kohn-Sham equations of density functional theory.

When evaluating the total ground-state energy in the Hartree Fock approximation for the one-particle orbitals of the free electron gas, the plane waves, the exchange term in the Hartree Fock equations causes an additional energy contribution which is called the exchange energy. It has the form $E_x/N = \frac{3e^2 k_F}{4\pi}$, where $k_F = (3\pi^2 n_0)^{1/3}$. In order to model exchange effects in interacting systems Slater suggested (1951,53) [8] to use the exchange contribution of the homogeneous electron gas but to replace the constant density n_0 by the actual local density $n(\mathbf{r})$ at the point $\mathbf{r}$ of the considered system. He used then for his calculations this additional potential in the form $v_x(\mathbf{r}) = \alpha \frac{e^2 (3\pi^2 n(\mathbf{r}))^{1/3}}{\pi}$ in a one-particle Schrödinger equation similar to the Hartree equations. To improve

numerical results the constant α often was varied but this had the notion of a somewhat arbitrary choice for the potential and lead to the discussion whether or not it is legitimate to work in an independent particle picture and if there is a unique effective one electron potential that corresponds to the considered interacting system. Because of the replacement of the constant density n_0 by the actual local $n(\mathbf{r})$, Slater's $X\alpha$ method can be viewed as precursor of the concept of the Local Density Approximation (LDA).

The contribution of Hohenberg and Kohn was to unify all these ideas and to give an exact framework for the theory which is based on the Hohenberg-Kohn theorem [1]. The theorem states that the ground-state density of a system of N-interacting electrons uniquely determines (to within an additive constant) the external potential of the system. As a consequence of the theorem, it can be concluded that the ground-state density completely determines all properties of the system such as the wavefunction, ground-state and excited-state energies, response properties, etc. Because of this one-to-one mapping, all the properties become then functionals of the ground state density. The Hohenberg-Kohn theorem gives no practical guide how to construct these functionals: it only ensures their uniqueness.

The one-to-one mapping between potentials and densities can be established for an arbitrary particle-particle interaction, including a vanishing interaction, i.e. for a system of non-interacting particles. This ensures the uniqueness of an effective one-particle potential which corresponds to the ground-state density of the interacting system. The publication of the proof in 1964 therefore stopped the discussion whether or not an effective single particle potential is a legitimate concept. Since the theorem guarantees the uniqueness of such a potential the focus was instead directed to the construction of good approximations for the (correct) effective one-particle potential.

1.1 Ground-state density functional theory

The static Hohenberg-Kohn theorem ensures that for every ground state density $n(\mathbf{r})$ which belongs to an interacting physical system of interest, there is an unique (if it exists) effective external potential $v_\mathrm{S}(\mathbf{r})$ for non-interacting particles with the same ground state density $n(\mathbf{r})$:

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2, \tag{1.1}$$

where the orbitals $\phi_i(\mathbf{r})$ come from an effective one-particle Schrödinger equation with the effective one-particle potential $v_\mathrm{S}(\mathbf{r})$

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + v_\mathrm{S}(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \varepsilon_i \, \phi_i(\mathbf{r}). \tag{1.2}$$

The system of non-interacting particles (Kohn-Sham system) is an auxiliary mathematical construct and the properties of this system like eigenfunctions and eigenvalues, Green's functions, response functions, etc. have a priori no direct physical meaning. The exception is the ground state density which is, by construction, equivalent in both systems, i.e. the interacting physical system of interest and the corresponding Kohn-Sham system of ficticious non-interacting particles. The ground-state energy functional is conventionally decomposed as

$$E[n] = T_\mathrm{S}[n] + \int d^3r \, v_\mathrm{ext}(\mathbf{r}) \, n(\mathbf{r}) + U[n] + E_\mathrm{XC}[n], \tag{1.3}$$

where $T_\mathrm{S}[n]$ is the kinetic energy functional for non-interacting electrons, the second term is the contribution of the external potential (usually due to the nuclei). The term $U[n]$ is the classical Hartree energy and $E_\mathrm{XC}[n]$ is the exchange-correlation energy functional which remains as the only piece to be approximated in practical applications. By defining the exchange-correlation potential as a functional derivative of the exchange-correlation energy functional

$$v_\mathrm{XC}[n](\mathbf{r}) = \frac{\delta \, E_\mathrm{XC}[n]}{\delta \, n(\mathbf{r})}, \tag{1.4}$$

a decomposition analogous to (1.3) can be obtained for the effective one-particle potential

$$v_\mathrm{S}(\mathbf{r}) = v_\mathrm{ext}(\mathbf{r}) + \int d^3r' \, \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_\mathrm{XC}[n](\mathbf{r}). \tag{1.5}$$

The effective potential v_{s} is by virtue of the Hohenberg-Kohn theorem a functional of the ground state density, so that eqns. (1.1,1.2, 1.5) have to be solved self-consistently. Accurate approximations for the unknown piece E_{XC} in the ground-state energy functional (1.3), or because of (1.4) for the unknown v_{XC} in the Kohn-Sham potential (1.5), have been devised since the advent of the theory. Modern GGA's typically predict the ground-state energy of an electronic system with an error less than 0.3 eV, bond lengths and angles are within 1% of experimental values and atomization energies typically have an absolute error of less than 0.3 eV [9], to mention just a few observable properties. In addition (1.5) shows that $v_{\mathrm{s}}[n](\mathbf{r})$ is a local potential, i.e. a multiplicative operator. This results in connection with the self-consistency scheme to a moderate scaling ($\sim N^3$) when the number of atoms N is increased. Hence, compared to other more expensive methods like configuration interaction or Møller-Plesset perturbation theory, density functional theory has become the most popular choice in chemistry for electronic structure calculations of medium sized and large systems.

1.2 Excitation energies in density functional theory

The Hohenberg-Kohn theorem ensures that every observable quantity of a physical system of interest is a functional of its ground-state density. Therefore all electronic excitation energies are also functionals of the ground-state density (e.g. $E_1[n_0]$ for the first excitation above the ground state). However, the theorem guarantees only the uniqueness of such functionals but gives no practical guideline how to construct them. In practice the most experience has been gained for the ground-state functional. Very accurate approximations for this energy functional have been devised and have found broad application in both physics and chemistry [10, 11].

In contrast to the developments for the ground-state energy functional very little is known about the functionals for the excited states of the system under consideration. Often the excitations of the auxiliary Kohn-Sham system are interpreted as physical excitations, such as in the band structure of solids [12], but this has no rigorous foundation and leads sometimes in practice to poor results especially for finite systems.

To date there are four distinct density functional based routes to excitation energies of

electronic systems which will be discussed briefly in the following sections.

1.2.1 Δ SCF approach to excitation energies

In the perhaps oldest approach known as ΔSCF [13], differences between ground state energies of excited configurations in the Kohn-Sham system are considered as approximation for the true excitation energies. For example the first excitation of the Beryllium atom would in this approach be obtained by evaluating the ground state energy functional at a self consistent density n_1 which corresponds to the excited configuration $1s^2 2s^1 2p^1$ and subtracting the ground-state energy of the Beryllium atom, i.e.

$$\Delta SCF \;=\; E_0[n_1] \;-\; E_0[n_0] \tag{1.6}$$

This is not quite correct since exchange and correlation pieces on the right hand side are evaluated at different densities n_1 and n_0.

1.2.2 Ensemble DFT

Another approach to excitation energies in DFT is through ensemble density functional theory [14, 15], where the ensemble density $n_{ensemble}$ is a weighted sum of the ground-state density and the density of the first excited-state

$$n_{ensemble} = w_0 \, n_0 \;+\; w_1 \, n_1 \tag{1.7}$$

The weights have to be chosen as

$$w_0 = \eta \quad w_1 = 1 - \eta, \quad \eta \geq \frac{1}{2} \tag{1.8}$$

to ensure that the ensemble density is normalized to N. The w_i can be chosen equal, i.e. $\eta = 1/2$, which is then called an equal ensemble or η can be adjusted by temperature to give a thermal ensemble. The ensemble energy has the form

$$\mathcal{E}(\eta) = (1 - \eta) \, E_0 + \eta \, E_1 \tag{1.9}$$

Note that (1.9) gives the ground-state energy for the choice $\eta = 0$. It follows from the general Rayleigh-Ritz principle for ensembles that the total-energy functional has the

variational properties

$$E^{(\eta)}[n_{ensemble}] = \mathcal{E}(\eta) \tag{1.10}$$

and

$$E^{(\eta)}[n] > \mathcal{E}(\eta) \quad \text{for} \quad n(\mathbf{r}) \neq n_{ensemble}(\mathbf{r}) \tag{1.11}$$

i.e. the exact ensemble energy $\mathcal{E}(\eta)$ can only be obtained for the exact ensemble density. For all other densities the inequality in (1.11) is strictly obeyed. By subtracting now $\mathcal{E}(\eta = 0)$ from (1.9) and dividing by η the first excitation energy can be calculated

$$\frac{1}{\eta}\left(\mathcal{E}(\eta) - \mathcal{E}(\eta = 0)\right) = E_1 - E_0 \tag{1.12}$$

This shows that the ensemble energy $\mathcal{E}(\eta)$ has to be known for only one value η with $\eta > 0$ to obtain together with the ground state energy $\mathcal{E}(\eta = 0)$ the first excitation energy. The scheme can be extended to ensembles of arbitrary size and to the case of degenerate levels [14]. Very little, however, is known about the particular dependence of the ensemble energy functional $E^{(\eta)}[n]$ on the parameter η and in practice the functional is replaced by LDA or a commonly used GGA ground-state energy functional [11].

1.2.3 Görling-Levy perturbation theory

Another possibility for the calculation of excitation energies is perturbation theory in the adiabatic coupling constant. The perturbation expansion starts with the Kohn-Sham Hamiltonian and the Kohn-Sham Slater determinant as the unperturbed Hamiltonian and wavefunction respectively. Since the non-interacting Kohn-Sham system and the corresponding interacting physical system have by construction the same density the perturbing Hamiltonian H_1 cannot simply be the electron-electron interaction. Turning on such an interaction would cause a density change in the system. In addition to the electron-electron interaction, one has therefore to apply a compensating external potential which ensures a fixed density for arbitrary values of the coupling constant λ [16, 17]. The particular form of the perturbing Hamiltonian in this Görling-Levy perturbation theory takes the form [18]

$$H^\lambda = H^0 + \lambda V_{ee} + \sum_{i=1}^{N}\left\{-\lambda u(\mathbf{r}_i) - \lambda v_{\mathrm{X}}(\mathbf{r}_i) - \frac{\delta E_{\mathrm{C}}^\lambda[n]}{\delta n(\mathbf{r}_i)}\right\} \tag{1.13}$$

By using the scaling relation for the correlation energy functional the last term can be expressed as

$$E_{\mathrm{C}}^{\lambda}[n] = \lambda^2 E_{\mathrm{C}}[n_{1/\lambda}] \tag{1.14}$$

and since this is already second order in the coupling constant the perturbing Hamiltonian is, in first order in λ, given by

$$H_1 = \hat{V}_{\mathrm{ee}} - \hat{U} - \hat{V}_{\mathrm{X}} \tag{1.15}$$

Here the abbreviation $\hat{U} = \sum_i^N u(\mathbf{r}_i)$ and $\hat{V}_{\mathrm{X}} = \sum_i^N v_{\mathrm{X}}(\mathbf{r}_i)$ was used. Ground state and excited state energies at full coupling $\lambda = 1$ may then be obtained by a coupling constant integration over the adiabatic connection parameter λ.

$$
\begin{aligned}
E_0(\lambda = 1) &= E_0(\lambda = 0) + \int_0^1 d\lambda \frac{dE_0}{d\lambda} \\
E_i(\lambda = 1) &= E_i(\lambda = 0) + \int_0^1 d\lambda \frac{dE_i}{d\lambda}
\end{aligned}
\tag{1.16}
$$

The difference of both are then an exact representation of the i-th excitation energy

$$\Omega_i(\lambda = 1) = E_i - E_0 = \varepsilon_i - \varepsilon_0 + \int_0^1 d\lambda \frac{d}{d\lambda}(E_i - E_0) \tag{1.17}$$

This can also be expressed in terms of matrix elements of the perturbing Hamiltonian

$$\Omega_i(\lambda = 1) = \varepsilon_i - \varepsilon_0 + \langle\, j\, |\, V_{\mathrm{ee}} - V_{\mathrm{X}} - V_{\mathrm{H}}\, |\, j\, \rangle - \langle\, 0\, |\, V_{\mathrm{ee}} - V_{\mathrm{X}} - V_{\mathrm{H}}\, |\, 0\, \rangle \tag{1.18}$$

1.2.4 Excitation energies from time-dependent DFT

The most popular density functional based approach to excitation energies is founded on TDDFT, the time-dependent extension of the original ground-state formalism. A recent calculation for the excitations of Chlorophyll α [19] shows that this scheme can be successfully applied to systems of even biological interest. The method is based on the fact that the frequency dependent density-density response of the physical system under consideration has poles at the exact excitation energies. In the scheme as proposed by Petersilka et al. [20], simple additive corrections shift the Kohn-Sham excitations towards the true physical excitations. The method will be discussed in detail in section 1.4. First, however, a discussion of the underlying time-dependent density functional formalism is necessary.

1.3   Time-dependent density functional theory

Most physical and chemical systems of interest are not static at all, instead they exhibit a highly dynamic behavior with frequently changing environments: complex scattering processes, atoms and molecules in time-dependent electromagnetic fields, the breaking and forming of chemical bonds, etc. All these examples require for their proper dynamical description, in principle, the full solution of the time-dependent many-particle Schrödinger equation. Because of the success of the ground-state DFT formalism a similar approach seems to be highly desirable for the general case of time-dependent external potentials caused by the more realistic environments mentioned above.

The first extensions of the ground-state density functional formalism were taken by Bartolotti (1981) [21] and Chakravarty (1979) [22]. In both cases the class of possible time-dependent external potentials was restricted to rather special forms (potentials periodic in time or potentials with a larger static and a smaller time-dependent part to be treated in linear response). The most general result proven to date for the time-dependent case is the Runge-Gross theorem [23]. It guarantees the existence of a one to one map between time-dependent external potentials and time-dependent densities. In particular it is shown that the time-dependent density of the system determines the (in general) time-dependent external potential up to a purely time-dependent function. This correspondence holds for an arbitrary particle-particle interaction especially for a vanishing interaction. A given time-dependent density $n(\mathbf{r}t)$ of an interacting system evolving under $v_{\mathrm{ext}}(\mathbf{r}t)$ therefore uniquely determines the external potential $v_{\mathrm{s}}(\mathbf{r}t)$ of non-interacting particles with the same density $n(\mathbf{r}t)$. The correspondence can, however, only be established if both systems evolve from a fixed initial many body state. This has the consequence that the potentials $v_{\mathrm{ext}}(\mathbf{r}t)$ and $v_{\mathrm{s}}(\mathbf{r}t)$ are not only functionals of the time dependent density $n(\mathbf{r}t)$ but depend also parametrically on their fixed initial many-body state Ψ and Φ. Similar to the static case it is then possible to formulate time dependent Kohn-Sham equations containing the effective one particle potential $v_{\mathrm{s}}(\mathbf{r}t)$. The TDKS equations take the form

$$i\hbar \frac{\partial}{\partial t}\phi_j(\mathbf{r}t) = \left(-\frac{\hbar^2 \nabla^2}{2m} + v_{\mathrm{s}}(\mathbf{r}t) \right) \phi_j(\mathbf{r}t) \qquad (1.19)$$

and the effective one particle potential may conventionally be written in the form

$$v_{\mathrm{S}}(\mathbf{r}t) = v_{\mathrm{ext}}(\mathbf{r}t) + \int d^3r' \frac{n(\mathbf{r}'t)}{|\mathbf{r}-\mathbf{r}'|} + v_{\mathrm{XC}}[n](\mathbf{r}t) \qquad (1.20)$$

The time-dependent exchange correlation potential is defined to make eqns. (1.19) and (1.20) exact but remains for practical applications the only unknown piece to be approximated. With orbitals resulting from (1.19), the time-dependent density is then constructed by

$$n(\mathbf{r}t) = \sum_{j=1}^{N} |\phi_j(\mathbf{r}t)|^2$$

The time-dependent Kohn-Sham scheme involves, however, contrary to the static case, no self consistency cycle. Instead equation (1.19) describes only the propagation of the chosen initial state in time.

To date most applications of the time-dependent Kohn-Sham formalism fall into the linear response regime [10, 24, 25]. In addition to a static potential $v_0(\mathbf{r})$, a time-dependent potential $v_1(\mathbf{r}t)$ is switched on at time t_1. The linear density response of the interacting system

$$n_1(\mathbf{r}t) = \int_{t_1}^{\infty} dt' \int d^3r' \, \chi(\mathbf{r}t, \mathbf{r}'t') v_1(\mathbf{r}'t') \qquad (1.21)$$

exposed to this potential can then be calculated as the linear density response

$$n_1(\mathbf{r}t) = \int_{t_1}^{\infty} dt' \int d^3r' \, \chi_{\mathrm{S}}(\mathbf{r}t, \mathbf{r}'t') v_{\mathrm{S}}^{(1)}(\mathbf{r}'t') \qquad (1.22)$$

of a system of non-interacting particles moving in an effective one particle potential. The effective time dependent potential $v_{\mathrm{S}}^{(1)}(\mathbf{r}t)$ to first order in the perturbing potential conventionally has the form

$$v_{\mathrm{S}}^{(1)}(\mathbf{r}t) = v_1(\mathbf{r}t) + \int d^3r' \frac{n_1(\mathbf{r}'t)}{|\mathbf{r}-\mathbf{r}'|} + \int dt' \int d^3r' f_{\mathrm{XC}}[n_0](\mathbf{r}t, \mathbf{r}'t') n_1(\mathbf{r}'t') \qquad (1.23)$$

The exchange-correlation kernel entering in (1.23) is defined as a functional derivative of the time-dependent exchange correlation potential

$$f_{\mathrm{XC}}[n_0](\mathbf{r}t, \mathbf{r}'t') = \frac{\delta v_{\mathrm{XC}}[n](\mathbf{r}t)}{\delta n(\mathbf{r}'t')}\Big|_{n=n_0} \qquad (1.24)$$

and the non-interacting response function can be expressed in terms of the Kohn-Sham orbitals

$$\chi_{\mathrm{S}}(\mathbf{r}, \mathbf{r}', \omega) = 2 \sum_{j,k} (n_k - n_j) \frac{\phi_k^*(\mathbf{r}) \phi_j(\mathbf{r}) \phi_j^*(\mathbf{r}') \phi_k(\mathbf{r}')}{\omega - \omega_{jk} + i\delta} \tag{1.25}$$

Given an approximation for the kernel f_{XC}, eqns. (1.22,1.23) may be used to self-consistently calculate the linear density response of the interacting system to the applied perturbation $v_1(\mathbf{r}t)$.

The idea of calculating excitation energies within the linear response regime of time-dependent density functional theory is based on the fact that the frequency-dependent linear density response of an interacting system has poles at the exact excitation energies of the system. Analogously the frequency dependent linear response function of a non-interacting (Kohn-Sham) system has poles at the Kohn-Sham excitations $\omega_{ij} = \varepsilon_i - \varepsilon_j$. Combining (1.21) and (1.23) leads to a relation between the interacting χ and the non-interacting response function χ_{S}. This is known as the Dyson-type equation for the linear response functions

$$
\begin{aligned}
\chi(\mathbf{r}, \mathbf{r}', \omega) &= \chi_{\mathrm{S}}(\mathbf{r}, \mathbf{r}', \omega) + \int d^3 r'' \int d^3 r''' \chi_{\mathrm{S}}(\mathbf{r}, \mathbf{r}', \omega) \\
&\times \left(\frac{1}{|\mathbf{r}'' - \mathbf{r}'''|} + f_{\mathrm{XC}}(\mathbf{r}'', \mathbf{r}''', \omega) \right) \chi(\mathbf{r}, \mathbf{r}', \omega)
\end{aligned} \tag{1.26}
$$

Here the kernel $f_{\mathrm{XC}}(\mathbf{r}'', \mathbf{r}''', \omega)$ is the Fourier transform of the functional derivative of the time-dependent exchange correlation potential.

One way to extract excitation energies and oscillator strengths from (1.26) is to solve, with some approximation for f_{XC}, the integral equation directly. It is then necessary to construct the non-interacting Kohn-Sham response function (1.25) from the corresponding orbitals $\phi_j(\mathbf{r})$ and Kohn-Sham eigenvalues ε_j. Usually the response functions are then expanded in a local basis set so that the solution of (1.26) becomes a matrix inversion problem [26]. This approach is rapidly becoming a standard tool in quantum chemistry and has been implemented in Gaussian 98 [19, 27, 28].

In practical applications different sources of errors enter in this direct solution of (1.26). Beside the truncation in the basis-set expansion the sum over all orbitals in (1.25) has to be truncated in some way or another. Even if these error sources are considered to

be small, the Kohn-Sham orbitals and excitation energies $\omega_{jk} = \varepsilon_j - \varepsilon_k$ which enter in (1.25) have to be calculated with an approximate form of the Kohn-Sham potential. Typical Kohn-Sham potentials resulting from an LDA or commonly used GGA energy functional exhibit, however, an incorrect asymptotic behavior as $r \to \infty$. This results in a missing Rydberg series and only a finite number of states are actually bound. If states and orbitals are simply missing they obviously cannot be included in the approximation for the Kohn-Sham response function which is then likely to cause poor approximations for χ_S. An improvement of this situation can be achieved by using OEP [32]-[37] potentials for which exchange is treated almost exactly, i.e. a Rydberg series is available in this case. Another source of errors is the approximation for the kernel f_{xc}. Commonly used exchange correlation kernels typically ignore the frequency dependence in f_{xc}. The approximations have however a minor relative importance compared to approximations for v_{xc}. [29]

1.4   Single pole approximation

A different approach to extract excitation energies from the integral equation (1.26) starts from the observation that the integral operator on the right of (1.26) has to become the unit operator at the exact excitations Ω_{ij} or equivalently

$$\int d^3r' \int d^3r'' \chi_S(\mathbf{r}, \mathbf{r}', \omega) \left(\frac{1}{|\mathbf{r} - \mathbf{r}''|} + f_{xc}(\mathbf{r}', \mathbf{r}'', \omega) \right) \zeta(\mathbf{r}''\omega) = \lambda(\omega)\, \zeta(\mathbf{r}\omega) \qquad (1.27)$$

where the eigenvalues $\lambda(\omega)$ have to satisfy $\lambda(\omega) = 1$ as $\omega \to \Omega_{ij}$. This constitutes an exact condition for the true excitations of the considered physical system. Petersilka et al. [20] use this condition to find resonances in the interacting response function directly. But there is no definite way to determine the nature of the poles, i.e., to distinguish for example between singlet and triplet excitations.

To actually calculate the excitation energies a Laurent expansion of (1.27) in the frequency variable around one particular Kohn-Sham pole ω_{ij} can be performed. The residuum $A(\omega_{ij})$ of the pole ω_{ij} in the expansion for the eigenvalue

$$\lambda(\omega) = \frac{A(\omega_{ij})}{\omega - \omega_{ij}} + B + (\omega - \omega_{ij})\, C + ... \qquad (1.28)$$

can then be obtained by a comparison with the corresponding Laurent expansion of the left hand side of (1.27). And with the exact condition $\lambda(\Omega_{ij}) = 1$ the expansion in (1.28) yields

$$
\begin{aligned}
1 \quad &= \quad \lambda(\Omega_{ij}) = \frac{A(\omega_{ij})}{\Omega_{ij} - \omega_{ij}} + B + ... \\
&\implies \quad \Omega_{ij} = \omega_{ij} + A(\omega_{ij}) + ...
\end{aligned}
\tag{1.29}
$$

which is a correction in lowest order for the Kohn-Sham excitations towards the true physical excitations. The expansion coefficient A in the Laurent series is given by

$$
A(\omega) = 2 \int d^3r \int d^3r' \phi_k(\mathbf{r})\phi_j^*(\mathbf{r}) \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}', \omega) \right) \phi_k^*(\mathbf{r}')\phi_j(\mathbf{r}')
\tag{1.30}
$$

which shows that beside an approximation for the exchange correlation kernel f_{xc}, only known quantities from a Kohn-Sham ground-state calculation are necessary to calculate the shifts of the Kohn-Sham excitations towards the physical excitations.

The single pole approximation (SPA) has several uses. It provides a very quick method for finding energy shifts without solving the full Dyson-type equation (1.26) or eigenvalue equation (1.27). The additive corrections for the Kohn-Sham excitations in (1.29) lead to quite accurate results for the excitations of the considered physical system [20],[30]. Perhaps more importantly, it allows us to see explicitly how approximations to the kernel f_{xc} influence the excitation shifts, and to understand how different approximations work. For example it has recently been shown [31] that these additive corrections for the excitations are equivalent to the energy corrections in first order Görling-Levy perturbation theory.

Chapter 2

Oscillator strengths from density functional theory

2.1 Oscillator strengths in atomic and molecular physics

When atomic or molecular systems interact with electromagnetic radiation, three different processes can appear. Similar to an oscillating classical charge distribution, an atom can radiate spontaneously. This spontaneous emission causes in the system a transition from an excited state to a state with lower energy. In an absorption process, the energy of the absorbed radiation allows a transition from a state of lower energy to a state of higher energy. And in the third possible process, stimulated emission, photons are emitted under the influence of an applied radiation field. All these processes can be characterized by the experimental accessible transition rates.

In a classical treatment of the electromagnetic field the time-dependent vector potential enters in the Hamiltonian. For the case of a weak radiation field, only linear terms in the vector potential need to be kept. The state of the system can then be expanded in the complete set of the eigenstates of the unperturbed Hamiltonian

$$\Psi(\mathbf{r}, t) = \sum_k c_k(t) \psi_k(\mathbf{r}) \tag{2.1}$$

The time dependent coefficients may be evaluated for the case of absorption in first order perturbation theory, yielding [7]

$$|c_b^{(1)}(t)|^2 = 2\pi \left[\frac{e A_0(\omega_{ab})}{m} \right]^2 |\langle \psi_b | e^{i\mathbf{k}\cdot\mathbf{r}} \epsilon \cdot \nabla | \psi_a \rangle|^2 t \tag{2.2}$$

In an ensemble of equivalent atomic or molecular systems under the same external conditions the probability $|c_b^{(1)}(t)|^2$ can be interpreted as the percentage of systems in the ensemble in the state b. The resulting probability (2.2) from first oder perturbation theory increases for small t linear with time so that the transition rate for absorption, i.e. the rate of systems in the ensemble changing to state b, can be defined as

$$W_{ba} = \frac{d}{dt} |c_b^{(1)}(t)|^2 = 2\pi \left[\frac{e A_0(\omega_{ab})}{m} \right]^2 |\langle \psi_b | e^{i\mathbf{k}\cdot\mathbf{r}} \epsilon \cdot \nabla | \psi_a \rangle|^2 \tag{2.3}$$

In the dipole approximation $(\mathbf{k} \cdot \mathbf{r}) \ll 1$ the series expansion of the exponent in (2.3) can be truncated after the constant term and one can use then the Heisenberg equation of motion to rewrite the matrix element

$$M_{ba} \approx \epsilon \cdot \langle\, \psi_b \,|\, \nabla \,|\, \psi_a \,\rangle = \epsilon \cdot \frac{im}{\hbar} \langle\, \psi_b \,|\, \dot{\mathbf{r}} \,|\, \psi_a \,\rangle = \frac{m}{\hbar^2}(E_a - E_b)\,\epsilon \cdot \langle\, \psi_b \,|\, \mathbf{r} \,|\, \psi_a \,\rangle \qquad (2.4)$$

Expressions similar to (2.3) may be obtained for spontaneous and stimulated emission. In every case, the transition rate is proportional to the dipole matrix element in (2.4). For the discussion of intensities it is therefore convenient to introduce a dimensionless quantity f_{ba} called oscillator strength

$$f_{ba} = \frac{2m\omega_{ba}}{3\hbar} |\langle\, \psi_b \,|\, \mathbf{r} \,|\, \psi_a \,\rangle|^2 \qquad (2.5)$$

The oscillator strength characterizes the intensity of a transition between two states a and b. From the definition it is clear that $f_{ba} > 0$ for absorption and $f_{ba} < 0$ for emission. It can be shown that the f_{ba} obey a sum rule due to Thomas, Reiche and Kuhn

$$\sum_a f_{ba} = 1 \qquad (2.6)$$

where the sum extends over all levels of the system including the continuum states. The definition allows us to rewrite the expressions for the transition rates of the system yielding, e.g., for spontaneous emission

$$W_{ba}^s = \frac{2\omega_{ba}^2}{mc^3}\left(\frac{e^2}{4\pi\varepsilon_0}\right)|f_{ba}| \qquad (2.7)$$

A quantity of interest related to the spontaneous emission is the lifetime of a level. If an atom or molecule is in an excited state and no external radiation field is applied, the only process which allows a transition to a state of lower energy is the spontaneous emission. The rate of change for a number of atoms $N(t)$ which are at time t in a particular level b is given by

$$\dot{N}_b(t) = N_b(t) \sum_k W_{kb}^s \qquad (2.8)$$

Since spontaneous emission is only possible to states of lower energy where the decay is allowed by the selection rule the summation in k extends only over these states.

Integrating this and relating the number of atoms at time t to the number at $t = 0$ by

$$N(t) = N(t = 0) \exp(-t/\tau_b) \tag{2.9}$$

the life-time or half-life of the level b can then be introduced

$$\tau_b^{-1} = \sum_k W_{kb}^s \tag{2.10}$$

In cases where the spontaneous emission to lower states is forbidden by the selection rules, the sum on the right hand side becomes zero yielding in the dipole approximation an infinite lifetime for this state. The simplest example for this would be the 2s level in atomic hydrogen. Here only higher order effects, e.g. simultaneous emission of two or more photons cause a finite lifetime for the level (see ref [7]).

The polarizability of atoms or molecules [38, 39] is a response property which is a measure for the induced dipole moment that the atom or molecule acquires when applied to an electric field. The induced dipole moment μ_z contains the permanent dipole moment of the atom or molecule (if there is one) and contributions induced by the electric field. It may be written as

$$\mu_z = \mu_{0,z} + \alpha_{zz} \mathcal{E} + \frac{1}{2} \beta_{zzz} \mathcal{E} \mathcal{E} + ... \tag{2.11}$$

For simplicity, the induced moment μ_z is assumed to be parallel to the applied field $\mathcal{E}_z$ in z-direction. In general, the electric field and the induced dipole moment have different spatial directions so that the coefficients in (2.11) become tensors of n-th order. The coefficient α is called polarizability and β is the first hyperpolarizability. The static polarizability for a system in state m can be obtained from standard perturbation theory [7]

$$\alpha = 2e^2 \sum_{\substack{n \\ n \neq m}} \frac{|\langle \psi_n \,|\, z \,|\, \psi_m \rangle|^2}{E_n - E_m} \tag{2.12}$$

And since this expression contains the expectation value of the dipole operator it can be expressed in terms of the oscillator strengths in (2.5)

$$\alpha = \frac{3e^2 \hbar}{m} \sum_{\substack{n \\ n \neq m}} \frac{f_{nm}}{(E_n - E_m)^2} \tag{2.13}$$

In general, however, the applied electric field is frequency dependent, so that polarizabilities and hyperpolarizabilities in (2.11) also become functions of the frequency variable. In this case, the response property $\alpha(\omega)$ has to be considered in first order time-dependent perturbation theory, or its equivalent the linear response formalism discussed in previous sections. In terms of the linear density response (1.22) of the considered atom or molecule, the frequency-dependent polarizability may be expressed as [40]

$$\alpha(\omega) = -\frac{2}{\mathcal{E}} \int d^3 r \, z \, n_1(\mathbf{r}\,\omega) = -\frac{2}{\mathcal{E}} \int d^3 r \int d^3 r' \, z \, \chi(\mathbf{r}, \mathbf{r}', \omega) \, v_1(\mathbf{r}'\,\omega) \qquad (2.14)$$

For particular frequencies atoms and molecules can absorb radiation and photoionize an electron. The polarizability (2.14) is in this case complex and the imaginary part gives the cross section for the photoionization [38]

$$\sigma(\omega) = \frac{4\pi\omega}{c} Im(\,\alpha(\omega)\,) \qquad (2.15)$$

The photoionization cross section obeys the f-sum rule [41]

$$\int_0^\infty \sigma(\omega) d\omega = \frac{2\pi Z e^2}{mc} \qquad (2.16)$$

or in other words, the area under the cross section is proportional to the number Z of electrons in the atom or molecule. This constraint is, in terms of the response functions, equivalent to the Thomas-Reiche-Kuhn sum rule (2.6). As it will be seen in the following sections, it is important that an approximation for the interacting response function obeys this sum rule. If this constraint is not respected, oscillator strengths in the spectrum are artificially added or removed and approximations for the transition rates poorly represent the physical reality.

The above discussion shows that the knowledge of the oscillator strengths for an atomic or molecular system allows us to determine the transition rates for absorption, spontaneous and stimulated emission and lifetimes of electronic levels as well as static polarizabilities. For the characterization of optical properties of atoms or molecules the oscillator strengths play, therefore, an important role.

2.2 Oscillator strengths from TDDFT

The definition for the oscillator strengths in the last section shows that the calculation of these quantities involves knowledge of both the excitation energies of the system and the excited wavefunctions corresponding to the considered levels. Neither are available in a ground state density functional formalism so that one has to take a different route to access oscillator strengths in a DFT based scheme.

A starting point can be the linear response formalism discussed in the last chapter. In practical calculations the oscillator strengths can be extracted from the pole strengths of the interacting response function. A solution of the Dyson-type equation (1.26) can be obtained by expanding the two point functions χ and χ_S in a localized basis set. The problem of solving for the interacting response function reduces then to a matrix inversion problem [26]. This method has recently been used by van Gisbergen et. al. [42].

2.3 The single pole approximation for oscillator strengths

2.3.1 Failures of a naive SPA

The promising results obtained in practical implementations of the SPA correction for excitation energies [19, 20, 26, 28] encourage an investigation of the same approximation for oscillator strengths. The oscillator strength belonging to a transition characterized by the excitation Ω_{ij} is determined by the pole strength of the interacting response function at this particular pole Ω_{ij}. The recipe for a correction would be at a first glance, similar to the case of excitation energies, to start from the Kohn-Sham response function and to systematically improve the Kohn-Sham pole strengths towards the true pole strengths of the interacting response function. A correction for the oscillator strengths can then be extracted from the corrected pole strengths in the approximation for χ. However, it turns out that this naive approach leads to a form of χ which does not conserve the sum rule for the photoionization cross section (2.16) or the equivalent Thomas Reiche Kuhn sum (2.6) rule for the extracted oscillator strengths. In this section, the violation is explicitly shown and the next section illustrates how to circumvent

the failure of such a naive single pole approximation.

The starting point for the discussion is the Dyson-type equation for the response functions (1.26)

$$\hat{\chi}(\omega) = \hat{\chi}_S(\omega) + \hat{\chi}_S(\omega)\,\hat{F}(\omega)\,\hat{\chi}(\omega) \tag{2.17}$$

All contributions are written in terms of operators so that no reference to an explicit representation is necessary and the shorthand $F \equiv F_{HXC}$ is used. Solving (2.17) now for $\hat{\chi}^{-1}$ yields

$$\hat{\chi}(\omega)^{-1} = \hat{\chi}_S(\omega)^{-1}\left[\hat{1} - \hat{\chi}_S(\omega)\,\hat{F}(\omega)\right] \tag{2.18}$$

The single pole approximation assumes a distinct separation of the poles in both response functions so that in the vicinity of a particular pole only one term contributes significantly. The Kohn-Sham response function (1.25) then becomes e.g.

$$\hat{\chi}_S^{SPA}(\omega) = 2(n_k - n_j)\frac{\hat{\Phi}_{jk} \otimes \hat{\Phi}_{jk}^*}{\omega - \omega_{jk} + i\delta} \equiv \frac{\hat{A}_{jk}}{\omega - \omega_{jk} + i\delta} \tag{2.19}$$

Inserting this in (2.18) gives

$$\begin{aligned}
\hat{\chi}(\omega)^{-1} &= (\omega - \omega_{jk} + i\delta)\,\hat{A}_{jk}^{-1}\left[\hat{1} - \frac{\hat{A}_{jk}}{\omega - \omega_{jk} + i\delta}\,\hat{F}(\omega)\right] \\
&= \hat{A}_{jk}^{-1}\left[(\omega - \omega_{jk} + i\delta)\hat{1} - \hat{A}_{jk}\hat{F}(\omega)\right]
\end{aligned} \tag{2.20}$$

It can be shown that, if the kernel F is frequency independent, the operator $\hat{A}_{jk}\hat{F}$ can assumed to be diagonal in the spatial variables with a degenerate eigenvalue a_{jk}. For simplicity, we may anticipate this result and abbreviate $\hat{A}_{jk}\hat{F} = a_{jk}\,\hat{1}$. The inverse of (2.20) becomes then

$$\hat{\chi}^{SPA}(\omega) = \frac{\hat{A}_{jk}}{\omega - \omega_{jk} - a_{jk} + i\delta} \tag{2.21}$$

The result shows that in the single pole approximation the position of the pole is shifted by a_{jk}, i.e. the Kohn-Sham excitation ω_{jk} (pole of the Kohn-Sham response function (2.19)) is corrected towards the physical excitation (pole of (2.21)). This is the known result discussed in section 1.4. However, the pole strength which corresponds to the transition $\Omega_{jk} \simeq \omega_{jk} + a_{jk}$ is equivalent to the pole strength of the Kohn-Sham

response function (2.19) at the Kohn-Sham pole ω_{jk}. In other words, the single pole approximation corrects the Kohn-Sham excitation towards the physical excitation but provides no correction for the pole strength of this excitation.

The expression in (2.21) holds for all Kohn-Sham poles provided a distinct separation from the neighboring poles is assumed. The approximation for the interacting response function then becomes

$$\hat{\chi}(\omega) \simeq \sum_{jk} \frac{\hat{A}_{jk}}{\omega - \omega_{jk} - a_{jk} + i\delta} \tag{2.22}$$

This is now readily seen to violate the sum rule (2.16). Evaluating the photoionization cross section (2.15) with (2.22) and integrating over frequency gives

$$
\begin{aligned}
\int_0^\infty \sigma(\omega)d\omega &= \frac{2\pi e^2}{c} \sum_{jk} (n_j - n_k)\,(\omega_{jk} + a_{jk})\,|\langle\, k\,|\,z\,|\,j\,\rangle|^2 \\
&= \frac{2\pi e^2}{mc} Z + \frac{2\pi e^2}{c} \sum_{jk} (n_j - n_k)\,a_{jk}\,|\langle\, k\,|\,z\,|\,j\,\rangle|^2 \tag{2.23}
\end{aligned}
$$

The shifts a_{jk} in the excitation energies cause an additional second term on the right hand side which violates the sum rule for the photoionization cross section (2.16). The reason for this behavior of the approximation in (2.22) is that only the poles in the response function are shifted while the pole strengths remain unchanged. While turning on the shifts a_{jk}, the pole strengths of the response function have to change in a proper way to compensate the effects of the a_{jk}. Hence, a more sophisticated single pole approximation has to account for a correction of both the poles of the response function and the corresponding pole strength.

2.3.2   Restoration of the sum-rule

To circumvent the violation of the sum rule caused by the naive SPA described in the last section a single pole approximation has to start from the operator $\omega\hat{\chi}$ instead of $\hat{\chi}$. Again a distinct separation between the poles is assumed. The approximate form of $\omega\,\chi_{\mathrm{s}}$ in the vicinity of the Kohn-Sham pole ω_{jk} is then

$$\omega\,\hat{\chi}_{\mathrm{s}} = \frac{\tilde{A}_{jk}}{w - w_{jk} + i\delta} \tag{2.24}$$

or equivalently

$$\hat{\chi}_S = \frac{\tilde{A}_{jk}}{(w - w_{jk} + i\delta)\,\omega} \tag{2.25}$$

To guarantee that this form of χ_S has at the pole ω_{jk} exactly the same residuum as $\hat{\chi}_S^{SPA}$ the operator $\tilde{A}_{jk}$ has to be chosen as

$$\lim_{\omega \to \omega_{jk}} (\omega - \omega_{jk})\hat{\chi}_S = \frac{\tilde{A}_{jk}}{\omega_{jk}} \equiv \hat{A}_{jk} = \lim_{\omega \to \omega_{jk}} (\omega - \omega_{jk})\hat{\chi}_S^{SPA} \tag{2.26}$$

Note that (2.25) exhibits at a certain distance away from the pole a different frequency dependence as (2.19). The relation in (2.26) ensures only that both are equivalent at the pole. This is vital since a correction of the pole strength has to start from the right point, i.e. the Kohn-Sham pole strength corresponding to ω_{jk}. Proceeding now in a similar fashion as in the last section and inserting (2.25) in the Dyson-type equation for the response functions to obtain

$$\hat{\chi}(\omega) = \frac{\tilde{A}_{jk}}{(w - w_{jk} - a_{ik} + i\delta)\,\omega} \tag{2.27}$$

The pole strength at the physical excitation is then

$$\alpha_{jk} = \lim_{\omega \to \omega_{jk} + a_{jk}} (\omega - \omega_{jk} - a_{jk})\,\chi(\omega) = \frac{\tilde{A}_{jk}}{w_{jk} + a_{ik}} = \frac{w_{jk}}{w_{jk} + a_{ik}}\,\hat{A}_{jk} \tag{2.28}$$

which allows the formulation of the approximate interacting response function

$$\hat{\chi}(\omega) \simeq \sum_{jk} \frac{w_{jk}}{w_{jk} + a_{ik}} \frac{\hat{A}_{jk}}{\omega - \omega_{jk} - a_{jk} + i\delta} \tag{2.29}$$

The additional factor in this approximation for $\hat{\chi}$ ensures now that the sum rule is preserved. This can be seen by evaluating the photoionization cross section and integrating over all frequencies

$$
\begin{aligned}
\int_0^\infty \sigma(\omega)\,d\omega &= \frac{2\pi e^2}{c} \sum_{jk} (n_j - n_k) \frac{w_{jk}}{w_{jk} + a_{ik}} \, (\omega_{jk} + a_{jk})\,|\langle\,k\,|\,z\,|\,j\,\rangle|^2 \\
&= \frac{2\pi e^2}{mc} Z \tag{2.30}
\end{aligned}
$$

The term $(w_{jk} + a_{ik})$ is exactly cancelled which restores the sum rule. A legitimation for the kind of operator for which the single pole approximation has to be performed can only be given in terms of the sum rule. One can imagine starting with a different

operator e.g. $\omega^n\,\chi$. However, the only choice for n which preserves the sum rule is $n = 1$. Although the pole strength is corrected with this modified single pole approximation the oscillator strengths which can be extracted from (2.28) do not change

$$
\begin{aligned}
f_{jk}^{phys} &= \frac{2}{3}\left(\omega_{jk} + a_{jk}\right)\alpha_{jk} = \frac{2}{3}\left(\omega_{jk} + a_{jk}\right)\frac{w_{jk}}{w_{jk} + a_{ik}}\,\hat{A}_{jk} \\
&= \frac{2}{3}\,w_{jk}\,\hat{A}_{jk} = \frac{2}{3}\,w_{jk}\,|\langle\,k\,|\,z\,|\,j\,\rangle|^2 \equiv f_{jk}^{KS}
\end{aligned}
\tag{2.31}
$$

It is therefore obvious why this approximation preserves the Thomas-Reiche-Kuhn sum rule. To get an explicit correction formula for the f values it is necessary to include more than one pole in the consideration from above. Work along these lines is in progress.

2.3.3   Spin decomposed SPA: Identifying the nature of excitations

The discussion so far has suppressed the spin-dependence of the response functions. The inclusion of spin degrees of freedom allows us to identify the nature of excitations. To illustrate this, consider (2.25) in spin form

$$
\hat{\chi}_{\mathrm{S}\sigma\sigma'} = \delta_{\sigma\sigma'}\frac{\tilde{A}_{jk\,\sigma\sigma'}}{(w - w_{jk} + i\delta)\,\omega}
\tag{2.32}
$$

Note that this is diagonal in spin space so that it can be treated as scalar. The Dyson-type equation has now to be extended to a (2x2) matrix equation

$$
\hat{\chi}_{\sigma\sigma'}(\omega)^{-1} = \hat{\chi}_{\mathrm{S}\sigma\sigma'}(\omega)^{-1}\left[\hat{1} - \hat{\chi}_{\mathrm{S}\sigma\sigma'}(\omega)\,\hat{F}_{\sigma\sigma'}(\omega)\right]
\tag{2.33}
$$

For spin saturated systems, $F_{\uparrow\uparrow} = F_{\downarrow\downarrow}$ and $F_{\uparrow\uparrow} = F_{\downarrow\downarrow}$ so that the insertion of (2.32) in (2.33) gives

$$
\hat{\chi}(\omega)^{-1} = \omega\,\hat{A}_{jk\,\sigma\sigma'}^{-1}
\begin{pmatrix}
(\omega - \omega_{jk} + i\delta) - \hat{A}_{jk,\uparrow\uparrow}\hat{F}_{\uparrow\uparrow}(\omega) & -\hat{A}_{jk,\uparrow\downarrow}\hat{F}_{\uparrow\downarrow}(\omega) \\
\hat{A}_{jk,\downarrow\uparrow}\hat{F}_{\downarrow\uparrow}(\omega) & (\omega - \omega_{jk} + i\delta) - \hat{A}_{jk,\downarrow\downarrow}\hat{F}_{\downarrow\downarrow}(\omega)
\end{pmatrix}
$$

Assuming now again a frequency independent kernel and abbreviating $A_{jk\,\sigma\sigma'}F_{\sigma\sigma'}(\omega) = a_{jk\sigma\sigma'}$ the inverse can be written

$$
\hat{\chi}(\omega) = \frac{\hat{A}_{jk\,\sigma\sigma'}}{((\omega - \omega_{jk} + i\delta - a_{jk\,\uparrow\uparrow})^2 - a_{jk\,\uparrow\downarrow}^2)\,\omega}
\begin{pmatrix}
(\omega - \omega_{jk} + i\delta) - a_{jk\,\uparrow\uparrow} & a_{jk\,\uparrow\downarrow} \\
a_{jk,\uparrow\downarrow} & (\omega - \omega_{jk} + i\delta) - a_{jk,\uparrow\uparrow}
\end{pmatrix}
$$

where we have used the fact that $a_{jk,\uparrow\uparrow} = a_{jk,\downarrow\downarrow}$ and $a_{jk,\downarrow\uparrow} = a_{jk,\downarrow\uparrow}$. The linear density-response for the spin densities is now in terms of the spin decomposed response function given by

$$\begin{pmatrix} n_{1,\uparrow} \\ n_{1,\downarrow} \end{pmatrix} = \begin{pmatrix} \chi_{\uparrow,\uparrow} & \chi_{\uparrow,\downarrow} \\ \chi_{\downarrow,\uparrow} & \chi_{\downarrow,\downarrow} \end{pmatrix} \begin{pmatrix} v_{1,\uparrow} \\ v_{1,\downarrow} \end{pmatrix} \tag{2.34}$$

Assume now the case of a spin independent perturbing potential $v_1(\mathbf{r}) = v_{1,\uparrow}(\mathbf{r}) = v_{1,\downarrow}(\mathbf{r})$. The total linear density response $n_1(\mathbf{r}) = n_{1,\uparrow}(\mathbf{r}) + n_{1,\downarrow}(\mathbf{r})$ can then be obtained from a scalar equation equivalent to (1.21) where the scalar linear response function χ has obviously to be taken as sum over all matrix elements in (2.34), i.e.

$$\hat{\chi}(\omega) = \sum_{\sigma\sigma'} \hat{\chi}_{\sigma\sigma'}(\omega) = \frac{2\hat{A}_{jk\,\sigma\sigma'}}{(\omega - \omega_{jk} - a_{jk\,\uparrow\uparrow} - a_{jk\,\uparrow\downarrow} + i\delta)\,\omega} \tag{2.35}$$

In the result only the spin decomposed excitation energies

$$\Omega_{jk} = \omega_{jk} + a_{jk\,\uparrow\uparrow} + a_{jk\,\uparrow\downarrow} \tag{2.36}$$

appear. Since the potential is spin-independent no spin-flip processes can occur and the excitations (2.36) can be assigned unambiguously to either singlet-singlet transitions or to triplet-triplet transitions (in both cases $\Delta S = 0$). All singlet-triplet excitations correspond to

$$\Omega_{jk} = \omega_{jk} + a_{jk\,\uparrow\uparrow} - a_{jk\,\uparrow\downarrow} \tag{2.37}$$

and have in this case a vanishing pole strength, i.e. are missing in (2.35).

2.4   Comparison with Görling-Levy perturbation theory

A possible second approach for a correction of the Kohn-Sham oscillator strengths is perturbation theory. The following considerations describe the first order correction for oscillator strengths in ordinary Schrödinger perturbation theory. The result is expressed in terms of matrix elements of the perturbing Hamiltonian so that no specific form for H_1 is assumed. By setting $H_1 = V_{\text{ee}}$, the ordinary perturbation theory would be obtained whereas a perturbation like (1.15) would correspond to Görling-Levy perturbation theory [18].

The first order correction for the states in terms of the unperturbed Slater determinants and energies is given by

$$
\begin{aligned}
\Psi_n^{(1)}(\mathbf{r}_1, ..., \mathbf{r}_n) &= \sum_{\substack{m \\ m \neq n}} \frac{\langle \Phi_n(\mathbf{r}_1, ..., \mathbf{r}_n) \mid H_1 \mid \Phi_m(\mathbf{r}_1, ..., \mathbf{r}_n) \rangle}{E_n^0 - E_m^0} \Phi_m(\mathbf{r}_1, ..., \mathbf{r}_n) \\
&= \sum_{\substack{m \\ m \neq n}} M_{nm} \Phi_m
\end{aligned}
\tag{2.38}
$$

where for ease of notation the abbreviation M_{mn} for the coefficients has been introduced. The first order correction for the energies with the above shorthand is simply

$$
E_n^{(1)} = M_{nn}
\tag{2.39}
$$

To construct oscillator strengths, the dipole matrix elements in first order in the coupling constant are necessary

$$
\langle \Phi_n + \lambda \Psi_n^{(1)} \mid \sum_j z_j \mid \Phi_m + \lambda \Psi_m^{(1)} \rangle
\tag{2.40}
$$

Inserting this and the perturbation expansion for the excitation energies in the definition of the oscillator strengths (2.5), the expansion for the transition rates becomes

$$
\begin{aligned}
f_{nm} &= \frac{2}{3} \omega_{nm} |\langle \Psi_n \mid \sum_j z_j \mid \Psi_m \rangle|^2 \\
&= \frac{2}{3}(E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ... - E_m^0 - \lambda E_m^{(1)} - \lambda^2 E_m^{(2)} - ...)(a_{nm} + \lambda b_{nm} + ...) \\
&= \frac{2}{3}(E_n^0 - E_m^0) a_{nm} + \frac{2}{3}\lambda(E_n^0 - E_m^0) b_{nm} + \frac{2}{3}(E_n^{(1)} - E_n(1)) a_{nm} + ... \\
&= f_{nm}^0 + \lambda c_{nm} + \lambda^2 d_{nm} + ...
\end{aligned}
\tag{2.41}
$$

With some algebra the correction matrix c_{nm} for the first order correction can be evaluated to give

$$
\begin{aligned}
c_{nm} = \frac{2}{3}(E_n^0 - E_m^0) &\left\{ \sum_{ij} \left(\sum_{\substack{l \\ l \neq n}} (A_{ml}^j M_{nl} A_{nm}^i + A_{lm}^j M_{nl} A_{mn}^i) \right. \right. \\
&\left. \left. + \sum_{\substack{l \\ l \neq m}} (A_{ln}^j M_{ml} A_{nm}^i + A_{nl}^j M_{ml} A_{mn}^i) + A_{nm}^j M_{nn} A_{mn}^i - A_{nm}^j M_{mm} A_{mn}^i \right) \right\}
\end{aligned}
\tag{2.42}
$$

Here the abbreviation $A_{nm}^i = \langle \Phi_n \, | \, z_i \, | \, \Phi_m \rangle$ has been used. By summing equation (2.41) over all states n, and using the fact that the oscillator strengths for the physical system, as well as the strengths for the Kohn-Sham system obey the sum rule, one obtains

$$
\begin{aligned}
\sum_n f_{nm} &= \sum_n f_{nm}^0 + \lambda \sum_n c_{nm} + \lambda^2 \sum_n d_{nm} \\
1 &= 1 + \lambda \sum_n c_{nm} + \lambda^2 \sum_n d_{nm} \\
0 &= \lambda \sum_n c_{nm} + \lambda^2 \sum_n d_{nm}
\end{aligned}
\tag{2.43}
$$

This is valid for arbitrary λ which leads to

$$
\sum_n c_{nm} = 0, \qquad \sum_n d_{nm} = 0, \qquad \dots
\tag{2.44}
$$

The same argument holds for the summation over m

$$
\sum_m c_{nm} = 0, \qquad \sum_m d_{nm} = 0, \qquad \dots
\tag{2.45}
$$

i.e. the sum of all elements in one row/column of the matrix c_{nm} is zero. In addition all diagonal elements of the matrix c_{nm} are zero which can directly be seen from (2.42) since in this case the energy prefactors vanish.

2.4.1   Special case: harmonic external potentials

In the last section all considerations have been general. Consider now as special example harmonic oscillators. Φ_n is then a Slater determinant of oscillator orbitals and since all oscillator eigenfunctions can be chosen to be real, the symmetry $A_{nm}^i = A_{mn}^i$ can be assumed. As a consequence, the first order correction for the oscillator strengths is proportional to A_{nm}^i (see (2.42)). The dipole operator can then be expressed by creation and annihilation operators for oscillator orbitals and one finally obtains

$$
\begin{aligned}
c_{nm} &\propto \sum_i A_{nm}^i = \langle \Phi_n \, | \sum_i z_i \, | \, \Phi_m \rangle \propto \langle \Phi_n \, | \sum_i (a_i + a_i^\dagger) \, | \, \Phi_m \rangle \\
&\propto \alpha_n \, \delta_{n,n+1} + \beta_n \, \delta_{n,n-1}
\end{aligned}
\tag{2.46}
$$

The diagonal of c_{nm} has already shown to be zero, so that the matrix c_{nm} has in this specific case the form

$$c = \begin{pmatrix} 0 & -u & & & \mathbf{0} \\ u & 0 & -v & & \\ & v & 0 & -w & \\ & & w & 0 & \ddots \\ \mathbf{0} & & & \ddots & \ddots \end{pmatrix} \qquad (2.47)$$

Applying now the sum rule $\sum_n c_{nm} = 0$ to the first column, i.e. $\sum_n c_{n1} = 0$ shows that $u = 0$. Application of the sum rule to the second column and usage of $u = -u = 0$ leads then to $v = 0$. This argument can be iterated which shows that all entries of the matrix are zero, i.e there is no first order correction in perturbation theory to the oscillator strengths when the Slater determinant Φ_n is composed of oscillator orbitals.

2.5   Numerical Results

2.5.1   Hooke's atom

To investigate the relationship between the Kohn-Sham oscillator strengths and their corresponding physical counterparts we have chosen a simple model system as a first test where the physical oscillator strengths can be evaluated analytically. Our choice, Hooke's atom [43, 44], consists of two interacting electrons exposed to a harmonic external potential. The oscillator strengths for this interacting system are simply those of a 3-D harmonic oscillator, since electromagnetic radiation couples in the dipole approximation only to the center of mass coordinate of the two electron system. In the Schrödinger equation for the Hooke's atom this coordinate however can be separated yielding a simple 3-D harmonic oscillator and showing therefore that the oscillator strengths for this system are equivalent to the strengths of the 3-D harmonic oscillator. These are readily evaluated from the known wavefunctions and energies (see Appendix D). The strengths for the 3-D oscillator are independent of the spring constant k as can be seen by a simple scaling argument when inserting the orbitals and energies in the definition of the oscillator strengths (2.5).

With the Kohn-Sham orbitals and energy eigenvalues, resulting from the exact Kohn-Sham potential (see Appendix B) of Hooke's atom with $k = \frac{1}{4}$, the expression in (2.5) was evaluated to obtain the Kohn-Sham oscillator strengths. Table (2.1) shows that

Transition	KS strengths	3-D oscillator	% deviation
0s − > 0p	0.9982115	1	0.179
1s − > 0p	-0.6647319	-0.6666667	0.291
1s − > 1p	1.6634432	1.6666667	0.194
2s − > 1p	-1.3316362	-1.3333333	0.127
2s − > 2p	2.3308559	2.3333333	0.106
3s − > 2p	-1.9986767	-2	0.066

Table 2.1: Oscillator strengths for the Kohn-Sham system of Hooke's atom at $k = \frac{1}{4}$ compared with the physical oscillator strengths of Hooke's atom which are those of a 3-D harmonic oscillator.

the Kohn-Sham oscillator strengths of Hooke's atom deviate only within approximately 0.3% from their physical counterparts. In figure (2.1), the oscillator strength f of the lowest allowed transition is plotted as a function of the non-interacting length scale $r_0 = (\frac{4}{k})^{(1/4)}$. In the high density limit of Hooke's atom ($r_0 \to 0$) the coulomb interaction between the two electrons becomes negligible compared to the dominating external potential so that the system behaves like two independent harmonic oscillators. In the case of two independent oscillators however, the first order correction in perturbation theory for the oscillator strengths vanishes (see argumentation in section 2.4.1). The non-interacting length scale is now a good measure for the coupling parameter λ. The almost parabolic shape of the curve in (2.1) for small values of r_0 is therefore consistent with a vanishing term to first order in λ. The fact that the correction vanishes to first order in λ is also the reason that the oscillator strengths of the Kohn-Sham system of Hooke's atom at $k = \frac{1}{4}$ are a very good approximation for their corresponding physical values. By going out to low values of the spring constant which correspond to increasing values for the length scale r_0 and similar to an increasing coupling parameter λ, the values for the oscillator strengths of the Kohn-Sham system begin to differ more distinctly from their corresponding physical values.
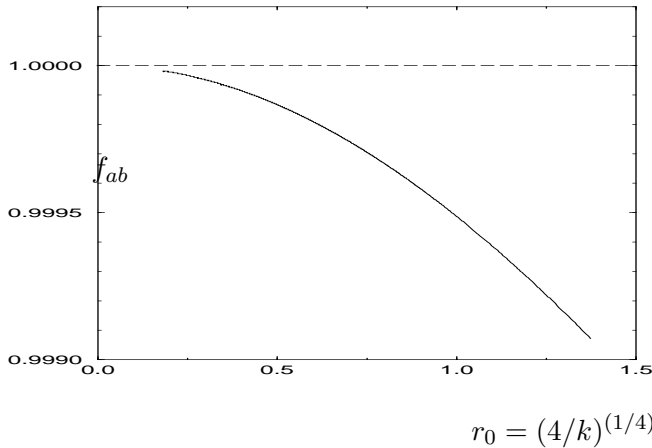

$$r_0 = (4/k)^{(1/4)}$$

Figure 2.1: transition 0s $\to$ 0p (allowed absorption for 3DO)

The vanishing first order correction for the oscillator strengths is however an artifact of the harmonic external potential, for general potentials there will be a first order

correction and the oscillator strengths in the Kohn-Sham system can differ significantly from their corresponding physical counterparts.

2.5.2   Helium isoelectronic series

For the calculation of oscillator strengths for the ions in the Helium isoelectronic series (Z=2,4,10,20,80), the numerically exact Kohn-Sham potentials for the ions have been employed [55]. The results summarized in the tables of this section show the Kohn-Sham oscillator strengths for the lowest 5 transitions out of the ground state into p levels. The Kohn-Sham oscillator strengths in Table 2.2 are compared with accurate nonrelativistic variational calculations from Ref. [51]. Similar to the spring constant in

transition	KS	He	KS	Be^{2+}	KS	Ne^{8+}
1s − > 2p	0.32429	0.27617	0.60824	0.55156	0.75183	0.72263
1s − > 3p	0.08473	0.07343	0.13359	0.12685	0.15070	0.14916
1s − > 4p	0.03407	0.02986	0.05099	0.04923	0.05610	0.05597
1s − > 5p	0.01708	0.01504	0.02494	0.02427	0.02712	0.02719
1s − > 6p	0.00976	0.00863	0.01408	0.01377	0.01522	0.01530
mean abs. dev.	14.7%		4.8%		1.2%	

Table 2.2: Oscillator strengths for the Kohn-Sham (KS) system of several ions in the Helium isoelectronic series. Lit. values taken from Ref. [51].

the case of Hooke's atom is here the nuclear charge Z the parameter, which models the adiabatic connection between interacting and noninteracting system. For $Z \to \infty$, the coulomb attraction of the core becomes dominant compared to the electron-electron repulsion, so that the electrons become essentially non-interacting in this limit. This is reflected in the fact that the oscillator strengths of the two-electron systems in the isoelectronic series approach twice the corresponding value of the hydrogen atom (i.e. non-interacting system) for increasing values of Z. The plot of the f-values as function of $1/Z$ illustrates this behavior. The Kohn-Sham oscillator strengths in the Kohn-Sham system lie always above but are approaching their physical counterparts while reaching the hydrogen limit as $1/Z \to 0$. (For a calculation of hydrogenic oscillator strengths see Appendix C).

transition	Ca^{18+}	Hg^{78+}	$2f_{ab}$ of Hydrogen
1s $->$ 2p	0.79900	0.82253	0.83239
1s $->$ 3p	0.15533	0.15736	0.15820
1s $->$ 4p	0.05729	0.05779	0.05798
1s $->$ 5p	0.02761	0.02780	0.02788
1s $->$ 6p	0.01547	0.01556	0.01560

Table 2.3: Oscillator strengths for the Kohn-Sham system (KS) of several ions in the Helium isoelectronic series. Lit. values taken from Ref. [51]. The last column shows the non-interacting limit (see Appendix C).

The calculation shows that the Kohn-Sham oscillator strengths are a good first estimate for their physical counterparts. All calculations were, however, performed with the exact Kohn-Sham potential which in realistic situations is only available in an approximate form. Kohn-Sham potentials resulting from commonly used LDA or GGA energy functionals exhibit the wrong asymptotic behavior which in turn causes poor approximations or even missing higher lying Kohn-Sham eigenvalues and orbitals. The oscillator strengths calculated from these approximate energies and orbitals are then obviously inferior to the exact KS values. It will be useful to explore the effects of approximations for the static Kohn-Sham potential on the oscillator strengths.
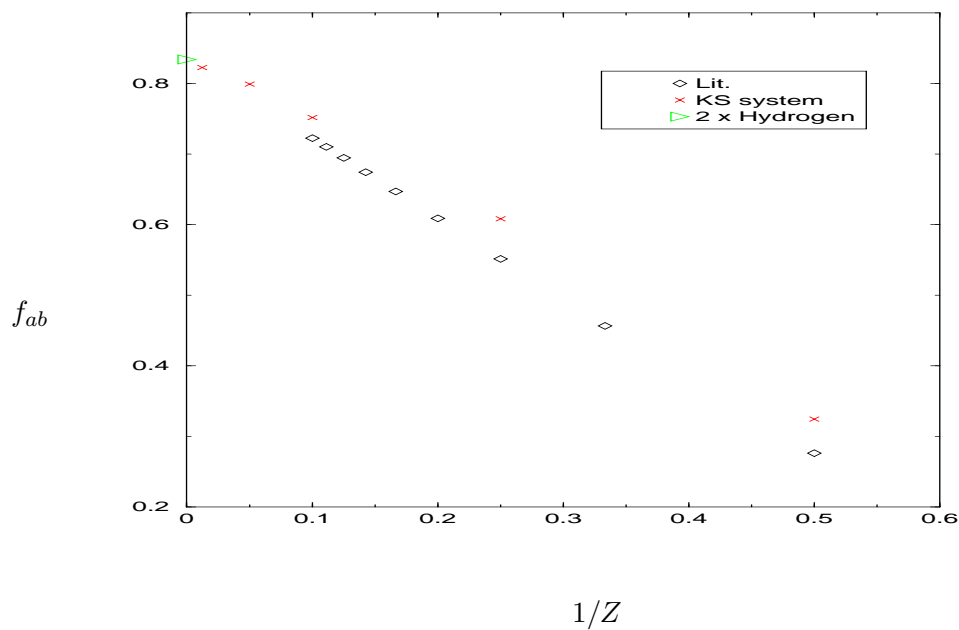
Figure 2.2: Transition 1s → 2p for the isoelectronic series compared to KS values

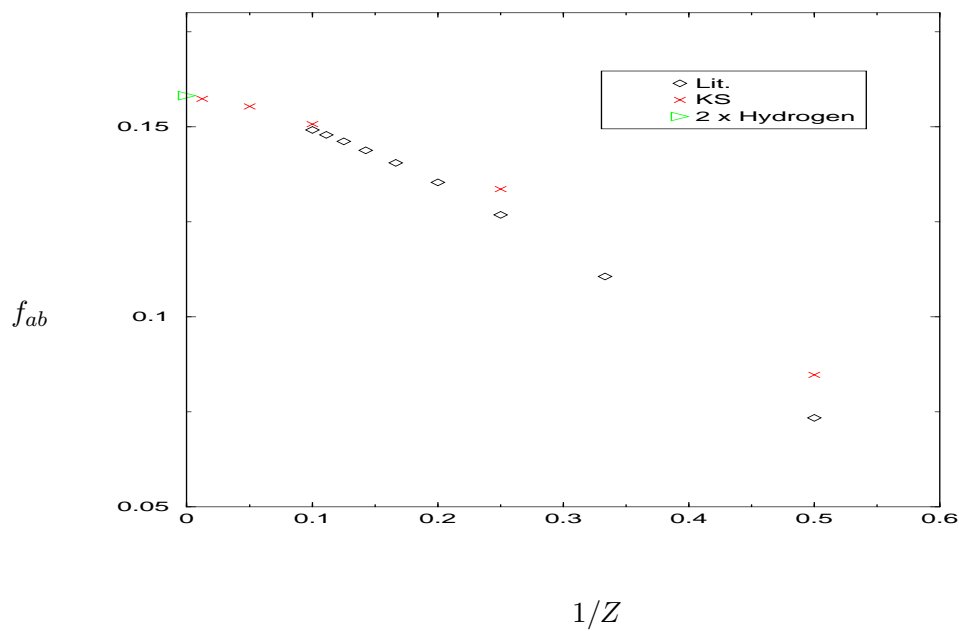Figure 2.3: Transition 1s → 3p for the isoelectronic series compared to KS values

Chapter 3

Conclusions and Outlook

3.1 New results

- We have presented a modified single pole approximation (SPA) for oscillator strengths which respects the Thomas-Reiche-Kuhn sum rule.

- We show that the correct single pole approximation does not alter the Kohn-Sham oscillator strengths.

- A spin-decomposed version of our SPA shows how to distinguish singlet and triplet transitions.

- We have calculated the Kohn-Sham and the exact oscillator strengths for the Hooke's atom.

- The Kohn-Sham oscillator strengths for several ions (Z=2,4,10,20,80) of the Helium isoelectronic series have been reported.

- The consideration of oscillator strengths in GL perturbation theory resulted in a first order correction expression. This result is for practical applications less suited because it contains sums over all states (continuum included) which causes difficulties in actually calculating these terms.

- The explicit form for the first order term allowed us, however, to prove that the first order correction for the oscillator strengths vanishes for systems exposed to harmonic external potentials.

3.2 Overall Conclusions

The Kohn-Sham oscillator strengths are an accurate first approximation to the exact physical oscillator strengths of the considered physical system. This is, however, only the case for the exact Kohn-Sham oscillator strengths. If approximate potentials, as in

every practical application employed, are used, the resulting oscillator strengths will be inferior to the exact Kohn-Sham values.

3.3   Work to be done

- It will be useful to consider simple ω-dependent models for the response functions, in order to investigate the validity of the approximations when more than one pole is considered. As a next step beyond a single pole approximation, the inclusion of two poles has to be examined. Since the single pole approximation is exact for infinitely separated poles, a double pole approximation will give a leading order correction if the poles are not infinitely far apart but, are well separated in the frequency domain. Similar to our modified single pole approximation, such a double pole approximation has, as important constraint, to satisfy the sum rule.

- Further insight may be gained, if the interacting response function can be expressed in terms of the eigenfunctions (1.27) and matrix elements (1.30) which appear in the single pole approximation to (1.26)

- Since all calculations, presented in this work, were done with the exact Kohn-Sham potentials, it will be interesting to compare them to the corresponding oscillator strengths which come from approximate potentials (e.g. LDA, GGA or OEP). We expect poor results, given the poor quality of the orbital energies in these approximations.

- It will be necessary to investigate, if the single pole approximation for the pole strengths is exact to first order. In this case there is no correction term in the parameter $1/Z$, i.e. the slopes of the physical and KS curve in Fig. 2.2 and 2.3 are identical for $1/Z \to 0$. A judgment cannot be made reliably with the results obtained so far.

Appendix A

Basis set expansion for Hooke's atom

The separation for the Schrödinger equation of Hooke's atom yields for the radial part of the relative coordinate the following radial equation

$$\left\{ -\frac{1}{u^2}\frac{\partial}{\partial u}u^2\frac{\partial}{\partial u} + \frac{l(l+1)}{u^2} + \frac{1}{4}ku^2 + \frac{1}{u} \right\} R_{nl}(u) = E\, R_{nl}(u) \tag{A.1}$$

This equation can be solved numerically e.g. by a basis-set expansion. One possible choice for the basis functions are gaussians multiplied by a power in u.

$$\begin{aligned} R_{nl}(u) &= \sum_j c_j \frac{1}{\pi^{3/4}u_0^{3/2}}\left(\frac{u}{u_0}\right)^j exp\left(-\frac{u^2}{2u_0^2}\right) \\ &= \sum_j c_j \langle\, u\,|\,j\,\rangle \end{aligned} \tag{A.2}$$

$$\langle\, u\,|\,j\,\rangle = \frac{1}{\pi^{3/4}u_0^{3/2}}\left(\frac{u}{u_0}\right)^j exp\left(-\frac{u^2}{2u_0^2}\right), \qquad u_0 = \sqrt{\frac{2}{\omega}} \tag{A.3}$$

At the values k, for the spring constant of the external potential, for which an analytical solution exists [43] this expansion collapses to a finite sum. It is therefore expected, that for values of k where no analytical solution is available the series converges rapidly, i.e. the expansion coefficients are expected to be sufficiently small for big j, so that a truncation can be performed without loss of accuracy. The set has also the advantage that all appearing matrix elements can be evaluated analytically:

- Overlap matrix element

$$\langle\, m\,|\,n\,\rangle = \frac{\Gamma\left(\frac{m+n+3}{2}\right)}{\Gamma\left(\frac{3}{2}\right)} \tag{A.4}$$

- Kinetic energy

$$\langle\, m\,|\, -\frac{1}{2}\nabla_{\mathbf{r}}^2\,|\,n\,\rangle = -\frac{\omega}{16}\left\{(m-n)^2 - 2(m+n) - 3\right\}\frac{\Gamma\left(\frac{m+n+1}{2}\right)}{\Gamma\left(\frac{3}{2}\right)} \tag{A.5}$$

- Centrifugal barrier potential

$$\langle\, m\,|\, \frac{l(l+1)}{2u^2}\,|\, n\,\rangle = -\frac{\omega}{4}\, l(l+1)\, \frac{\Gamma\left(\frac{m+n+1}{2}\right)}{\Gamma\left(\frac{3}{2}\right)} \tag{A.6}$$

- Oscillator potential

$$\langle\, m\,|\, \frac{1}{2}\, k\, u^2\,|\, n\,\rangle = \frac{\omega}{4}\, \left\{(m+n)^2 + 4(m+n) + 3\right\}\, \frac{\Gamma\left(\frac{m+n+1}{2}\right)}{\Gamma\left(\frac{3}{2}\right)} \tag{A.7}$$

- Particle-particle interaction

$$\langle\, m\,|\, \frac{1}{u}\,|\, n\,\rangle = \left(\frac{\omega}{2}\right)^{\frac{1}{2}}\, \frac{\Gamma\left(\frac{m+n+2}{2}\right)}{\Gamma\left(\frac{3}{2}\right)} \tag{A.8}$$

Appendix B

Sternheimer method and analytic form for the Kohn-Sham potential of Hooke's atom

For a system with two non-interacting electrons the ground-state density is simply given by

$$n(\mathbf{r}) = \sum_{i=1}^{2} |\phi_i(\mathbf{r})|^2 = 2|\phi(\mathbf{r})|^2 \tag{B.1}$$

One can solve this for the orbital $\phi(\mathbf{r})$ and invert the Kohn-Sham equation to express the effective one particle potential in terms of the ground state density. Some straightforward algebra leads to

$$
\begin{aligned}
v_{KS} &= E + \frac{1}{2\phi(\mathbf{r})} \Delta\phi(\mathbf{r}) \\
&= E - \frac{1}{2}\left(\frac{\nabla n(\mathbf{r})}{2n(\mathbf{r})}\right)^2 + \frac{1}{4}\frac{\Delta n(\mathbf{r})}{n(\mathbf{r})}
\end{aligned} \tag{B.2}
$$

The two electron model system "Hooke's atom" can be solved analytically for an infinite but discrete set of values for the spring constant k of the external potential [43]. The ground state density at $k = \frac{1}{4}$ is for example given by [44]

$$n(\mathbf{r}) = \frac{\pi\sqrt{2\pi}}{4\pi^{5/2}(5\sqrt{\pi}+8)r}\exp\left(-\frac{r^2}{2}\right)\left[7r + r^3 + \frac{8}{\sqrt{2\pi}}r\,\exp\left(-\frac{r^2}{2}\right)\right.$$
$$\left. +4(1+r^2)\,erf\left(\frac{r}{\sqrt{2}}\right)\right] \tag{B.3}$$

By inserting this result in the above relation (B.2) an analytical expression for the Kohn-Sham potential of Hooke's atom ($k = \frac{1}{4}$) can be obtained

$$
\begin{aligned}
v_{KS}(\mathbf{r}) = &\left\{32\,r^2\left(-1 - 8\,r^2 + r^4\right) + 8\,e^{\frac{r^2}{2}}\sqrt{2\pi}\,r\left(r^3\left(-45 - 2\,r^2 + r^4\right) + 4\left(1 - 5\,r^2\right.\right.\right. \\
&\left.\left.-7\,r^4 + r^6\right)erf(\frac{r}{\sqrt{2}})\right) + e^{r^2}\pi\left(r^4\left(-210 - 55\,r^2 + 4\,r^4 + r^6\right) +\right. \\
&8\,erf(\frac{r}{\sqrt{2}})\left(r^3\left(-13 - 43\,r^2 - r^4 + r^6\right) + 2\left(-1 + 2\,r^2 - 8\,r^4 - 6\,r^6 + r^8\right)\right. \\
&\left.\left.erf(\frac{r}{\sqrt{2}})\right)\right\} / \left\{8\,\pi\,r^2\left(4\sqrt{\frac{2}{\pi}}\,r + e^{\frac{r^2}{2}}\left(r\left(7 + r^2\right) + 4\left(1 + r^2\right)erf(\frac{r}{\sqrt{2}})\right)\right)^2\right\}
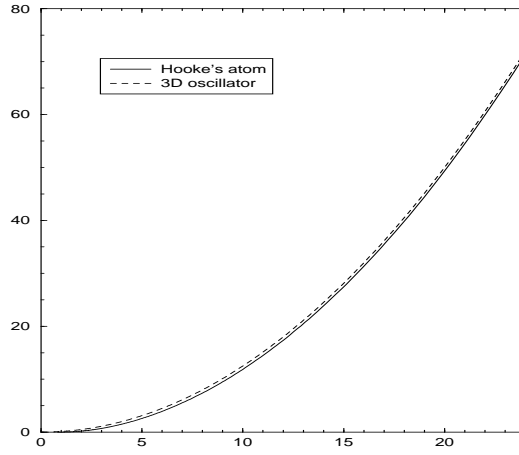\end{aligned} \tag{B.4}
$$

Figure B.1: KS potential of Hooke's atom compared with the 3D Oscillator potential

An asymptotic expression can be found in Ref. [57], and an exact expression for the correlation potential is given in Ref. [56]. The Hartree and exchange potentials for two electron systems are simply related and since the ground state density in (B.3) is spherically symmetric both can be evaluated by an integral over the radial coordinate

$$v_{\mathrm{H}}(\mathbf{r}) = -\frac{1}{2}v_{\mathrm{X}}(\mathbf{r}) = \int d^3r' \frac{n(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} = 4\pi \int dr\, r^2\, n(r)\frac{1}{r_>} \tag{B.5}$$

$$v_{\mathrm{H}}(r) = \frac{1}{(8+5\sqrt{\pi})\, r}\left\{16\, erf(r) - \sqrt{2}\left(r + 12\, erf(\frac{r}{\sqrt{2}})\right)\exp(-\frac{r^2}{2})\right.$$
$$\left. +2\sqrt{\pi}\left(2\, r + erf(\frac{r}{\sqrt{2}})\left(5 - 2\, r\, erf(\frac{r}{\sqrt{2}})\right)\right)\right\} \tag{B.6}$$
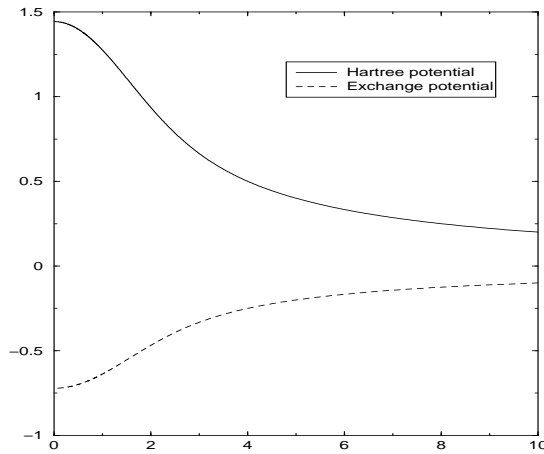

Figure B.2: Hartree and exchange potential for Hooke's atom

Appendix C

Oscillator strengths for the hydrogen atom

Since the wavefunction in this particular case is known analytically [7]

$$\psi(\mathbf{r}) = -\left\{ \left(\frac{2Z}{na_\mu}\right)^3 \frac{(n-l-1)!}{2\,n\,[(n+l)!]^3} \right\}^{1/2} \exp(-\rho/2)\, r^l\, L_{n+l}^{2l+1}(\rho)\, Y_{lm}(\theta,\phi) \qquad \text{(C.1)}$$

where

$$\rho = \frac{2Z}{na_\mu}, \qquad a_\mu = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2} \qquad\qquad \text{(C.2)}$$

the oscillator strengths $f_{ab} = \frac{2\,\omega_{ab}}{3}|\langle\, a\,|\,z\,b\,\rangle|^2$ may be evaluated exactly, yielding simple fractions for the transition rates within the dipole approximation. The table below gives the result for allowed transitions between the lowest s and p levels.

The calculations of the oscillator strengths for the hydrogen atom were performed with MATHEMATICA [61]. The required Notebook can be retrieved from my webpage [62].

	2p	3p	4p	5p	6p	7p	8p
1s	-0.41620	-0.07910	-0.02899	-0.01394	-0.00780	-0.00481	-0.00318
2s	0	-0.43487	-0.10277	-0.04193	-0.02163	-0.01274	-0.00818
3s	0.04077	0	-0.48471	-0.12102	-0.05139	-0.02737	-0.01655
4s	0.00913	0.09675	0	-0.54415	-0.13812	-0.05965	-0.03227
5s	0.00364	0.02228	0.15872	0	-0.60776	-0.15488	-0.06737
6s	0.00185	0.00910	0.03701	0.22361	0	-0.67356	-0.17153
7s	0.00108	0.00474	0.01528	0.05248	0.29015	0	-0.74065
8s	0.00069	0.00282	0.00805	0.02180	0.06835	0.35770	0

Table C.1: Oscillator strengths for transitions in atomic hydrogen

Appendix D

Oscillator strengths for the 3-D harmonic oscillator

Analogous to the case of atomic hydrogen, the 3-D oscillator is exactly solvable so that the oscillator strengths can be evaluated analytically. The wavefunction of the oscillator in spherical coordinates is given by [49, 50]

$$\psi(\mathbf{r}) = C \, r^l \exp(-\frac{\sqrt{k}}{2} r^2) \, {}_1F_1(-n_r, l+3/2; \sqrt{k}r^2) \, Y_{l,m}(\theta, \phi) \tag{D.1}$$

Here, ${}_1F_1$, is the hypergeometric function in the standard notation. The oscillator has, in addition to the selection rules for atomic potentials, a further selection rule. This is due to the fact that the dipole operator can be expressed in terms of creation and annihilation operators for the oscillator quanta. Matrix elements of this operator connect only states with $\Delta(2n+l) = \pm 1$

$$f_{ij} = \frac{2}{3}\omega_{ij}|\langle\, i\,|\,z\,|\,j\,\rangle|^2 = \frac{2}{3}\omega_{ij}|\langle\, i\,|\,\frac{(a+a^\dagger)}{(4k)^{\frac{1}{4}}}\,|\,j\,\rangle|^2 \tag{D.2}$$

The calculations of the oscillator strengths for the 3-D oscillator were performed with MATHEMATICA [61]. The required Notebook can be retrieved from my webpage [62].

	0p	1p	2p	3p	4p	5p	6p
0s	-1	0	0	0	0	0	0
1s	$\frac{2}{3}$	$-\frac{5}{3}$	0	0	0	0	0
2s	0	$\frac{4}{3}$	$-\frac{7}{3}$	0	0	0	0
3s	0	0	2	-3	0	0	0
4s	0	0	0	$\frac{8}{3}$	$-\frac{11}{3}$	0	0
5s	0	0	0	0	$\frac{10}{3}$	$-\frac{13}{3}$	0
6s	0	0	0	0	0	4	-5
7s	0	0	0	0	0	0	$\frac{14}{3}$

Table D.1: Oscillator strengths for the 3-D harmonic oscillator

Appendix E

Implementation of the SPA correction for excitation energies

The correction of the Kohn-Sham excitation energies towards the excitations of the corresponding physical system within the TDDFT approach are given by [20]

$$\Omega_{jk} = \omega_{jk} + Re(M_{jk,jk}) \tag{E.1}$$

where the matrix elements $M_{jk,jk}$ have the form

$$\begin{aligned}
M_{jk,jk} &= 2(n_k - n_j) \int d^3r \int d^3r' \, \phi_k(\mathbf{r})\phi_j^*(\mathbf{r}) \\
&\times \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}', \omega) \right) \phi_k^*(\mathbf{r}')\phi_j(\mathbf{r}')
\end{aligned} \tag{E.2}$$

In any practical calculation an approximation for the kernel f_{xc} has to be made. A particularly simple form can be obtained from the time dependent optimized effective potential method [32]-[37]

$$f_{\mathrm{xc}}[n_0](\mathbf{r}, \mathbf{r}, \omega) = -\frac{2|\sum_k n_k \phi_k(\mathbf{r})\phi_k^*(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'| \, n_0(\mathbf{r})n_0(\mathbf{r}')} \tag{E.3}$$

The result shows that the frequency dependence of the kernel is completely ignored in this approach. For the case of a two electron systems treated within a TD exchange-only theory, this becomes exact and can be further reduced to

$$f_{\mathrm{xc}}[n_0](\mathbf{r}, \mathbf{r}, \omega) = -\frac{1}{2|\mathbf{r} - \mathbf{r}'|} \tag{E.4}$$

Assuming, furthermore, the form

$$\phi_{n,l,m}(\mathbf{r}) = R_n(r)Y_l^m(\theta, \phi) \tag{E.5}$$

for the Kohn-Sham orbitals and using for the coulomb operator the expansion, in terms of associated Legendre functions,

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{r_>} \sum_{n=0}^{\infty} \left(\frac{r_<}{r_>} \right)^n P_n(\cos(\theta)) \tag{E.6}$$

the matrix elements in (E.2) can be written as

$$M_{jk,jk} = -\frac{1}{2}(n_k - n_j) \sum_{i=0}^{\infty} I^i_{n,n',l,l'} \, b_i(l,m,l',m') \qquad (E.7)$$

Here the b_i are Slater coefficients (see Appendix F) and the integrals $I^i_{n,n',l,l'}$ are given by

$$\begin{aligned}
I^i_{n,n',l,l'} &= \int_0^{\infty} r^2 dr \int_0^r r'^2 dr' \left(\frac{r'}{r}\right)^i \frac{1}{r} R_{nl}(r), R^*_{n'l'}(r), R^*_{nl}(r'), R_{n'l'}(r') \\
&+ \int_0^{\infty} r^2 dr \int_r^{\infty} r'^2 dr' \left(\frac{r}{r'}\right)^i \frac{1}{r'} R_{nl}(r), R^*_{n'l'}(r), R^*_{nl}(r'), R_{n'l'}(r') \quad (E.8)
\end{aligned}$$

Appendix F

Integrals of the product of three spherical harmonics and Slater coefficients

Integrals of the product of three spherical harmonics appear in the calculation of oscillator strengths as well as in the calculation of matrix elements in perturbation theory. Conventionally they can be written as Slater coefficients (see Ref. [48])

$$b_k(l_1, m_1, l_2, m_2) = \frac{4\pi}{2k+1} \left[\int d\Omega \, Y_{l_2}^{m_2 \, *} Y_k^{m_2 - m_1} Y_{l_1}^{m_1} \right]^2 \tag{F.1}$$

A simple way to evaluate these coefficients may be obtained by their relation to Clebsch-Gordan coefficients

$$\int d\Omega \, Y_{l_1}^{m_1} Y_{l_2}^{m_2} Y_{l_3}^{m_3} = (-1)^{m_3} \left(\frac{(2l_1+1)(2l_2+1)}{4\pi(2l_3+1)} \right)^{\frac{1}{2}} \langle \, l_1 l_2 00 \, | \, l_3 0 \, \rangle \langle \, l_1 l_2 m_1 m_2 \, | \, l_3 - m_3 \, \rangle \tag{F.2}$$

Using then the relation

$$Y_l^{-m}(\theta, \phi) = (-1)^m Y_l^{m*}(\theta, \phi) \tag{F.3}$$

the Slater coefficients can finally be expressed as

$$b_k(l_1, m_1, l_2, m_2) = \frac{2l_1 + 1}{2l_2 + 1} \left[\langle \, l_1 k 00 \, | \, l_2 0 \, \rangle \langle \, l_1 k m_1 m_2 - m_1 \, | \, l_2 m_2 \, \rangle \right]^2 \tag{F.4}$$

References

[1] *Inhomogeneous electron gas*, P. Hohenberg and W. Kohn, Phys. Rev. **136**, B 864 (1964).

[2] *Self-consistent equations including exchange and correlation effects*, W. Kohn and L.J. Sham, Phys. Rev. **140**, A 1133 (1965).

[3] D.R. Hartree, Proc. Cambridge Phil. Soc. **24**, 89 (1928)

[4] V. Fock, Z. Phys. **61**, 126 (1930)

[5] E.K.U. Gross, E. Runge, and O. Heinonen, *Many-Particle Theory* (Adam Hilger, Bristol, 1991).

[6] A. Szabo and N. S. Ostlund *Modern quantum chemistry: introduction to advanced electronic structure theory* (Macmillan, New York, 1982)

[7] B. H. Bransden and C.J. Joachain *Physics of atoms and molecules* (Longman, Essex, 1983)

[8] J.C. Slater, Phys. Rev. **81**, 385 (1951); **82**, 538 (1951); **91**, 52 (1953)

[9] *Density functionals for non-relativistic Coulomb systems*, J.P. Perdew and S. Kurth, in *Density functionals: Theory and applications*, ed. D. Joubert (Springer, Berlin, 1998).

[10] *Density Functional Theory*, Vol. 337 *NATO ASI Series B*, edited by E.K.U. Gross and R.M. Dreizler (Plenum Press, New York, 1995)

[11] *Nonlocal density functionals for exchange and correlation: Theory and applications*, K. Burke, J. P. Perdew, and M. Levy, in *Modern Density Functional Theory: A Tool for Chemistry*, edited by J. M. Seminario and P. Politzer (Elsevier, Amsterdam, 1995).

[12] N.W. Ashcroft and N.D. Mermin, *Solid State Physics* (Holt, Rinehart, and Winston, NY, (1976).

[13] *On the calculation of multiplet energies by the Hartree-Fock-Slater method*, T. Ziegler, A. Rauk, and E. J. Baerends, Theoret. Chim. Acta **43**, 261 (1977).

[14] *Density-functional theory for ensembles of fractionally occupied states. I. Basic formalism*, E.K.U. Gross, L.N. Oliveira, and W. Kohn, Phys. Rev. A **37**, 2809 (1988).

[15] E.K.U. Gross, L.N. Oliveira, and W. Kohn, Phys. Rev. A **37**, 2805 (1988).

[16] *The exchange-correlation energy of a metallic surface*, D.C. Langreth and J.P. Perdew, Solid State Commun. **17**, 1425 (1975).

[17] O. Gunnarsson and B.I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[18] *Correlation-energy functional and its high-density limit obtained from a coupling-constant perturbation expansion*, A. Görling and M. Levy, Phys. Rev. B **47**, 13105 (1993).

[19] *Density functional theory calculations of the visible spectrum of chlorophyll* α D. Sundholm, Chem. Phys. Lett. **302**, 480 (1999)

[20] *Excitation energies from time-dependent density-functional theory*, M. Petersilka, U.J. Gossmann, and E.K.U. Gross, Phys. Rev. Lett. **76**, 1212 (1996).

[21] L.J. Bartolotti, Phys. Rev. A **24**, 1661 (1981); **26**, 2243 (1982).

[22] S. Chakravarty, M.B. Fogel and W. Kohn, Phys. Rev. Lett. **43**, 775 (1979).

[23] *Density-functional theory for time-dependent systems*, E. Runge and E.K.U. Gross, Phys. Rev. Lett. **52**, 997 (1984).

[24] *Local density-functional theory of frequency-dependent linear response*, E.K.U. Gross and W. Kohn, Phys. Rev. Lett. **55**, 2850 (1985); **57**, 923 (1986) (E).

[25] *Time-dependent optimized effective potential in the linear response regime*, M. Petersilka, U.J. Gossmann, and E.K.U. Gross, in *Electronic Density Functional Theory: Recent Progress and New Directions*, eds. J.F. Dobson, G. Vignale, and M.P. Das (Plenum, NY, 1997).

[26] *Treatment of electronic excitations within the adiabatic approximation of time-dependent density functional theory* R. Bauernschmitt and R. Ahlrichs, Chem. Phys. Lett. **256**, 454 (1996)

[27] *Dynamic polarizabilities and excitation spectra from a molecular implementation of time-dependent density functional response theory: N_2 as a case study*, C. Jamorski, M.E. Casida, D.R. Salahub, J. Chem. Phys. **104**, 5134 (1996).

[28] *Time-dependent density functional theory for radicals. An improved description of excited states with substantial double exciation character* S. Hirata and M. Head-Gordon, Chem. Phys. Lett. **302**, 375 (1999)

[29] *Excitation energies from time-dependent density functional theory using exact and approximate potentials* M. Petersilka, K. Burke and E.K.U. Gross, in prep.

[30] *Spin-multiplet energies from time-dependent density functional theory* M. Petersilka and E.K.U. Gross, Int. J. Quantum Chem. S **30**, 1393 (1996).

[31] *Exchange and Correlation Kernels at the Resonance Frequency: Implications for Excitation Energies in Density-Fuctional Theory* X. Gonze and M. Scheffler, Phys. Rev. Lett. **82**, 4416 (1999).

[32] *A Variational approach to the unipotential many-electron problem*, R.T. Sharp and G.K. Horton, Phys. Rev. **90**, 317 (1953).

[33] J.D. Talman and W.F. Shadwick, Phys. Rev. A **14**, 36 (1976).

[34] *Construction and application of an accurate local spin-polarized Kohn-Sham potential with integer discontinuity: Exchange-only theory*, J.B. Krieger, Y. Li, and G.J. Iafrate, Phys. Rev. A **45**, 101 (1992).

[35] J. B. Krieger, Y. Li, and G. J. Iafrate, Phys. Rev. A **46**, 5453 (1992).

[36] *Time-dependent optimized effective potential*, C.A. Ullrich, U.J. Gossman, and E.K.U. Gross, Phys. Rev. Lett. **74**, 872 (1995).

[37] *Density-functional theory using an optimized exchange-correlation potential* T. Grabo and E.K.U. Gross, Chem. Phys. Lett. **240**, 141 (1995); **241**, 635(E) (1995).

[38] *Local Density Theory of Polarizability*, G.D. Mahan and K.R. Subbaswamy, (Plenum Press, New York, 1990).

[39] *Molecular Quantum Mechanics* P.W. Atkins and R.S. Friedmann, (Oxford University Press, Oxford, 1997)

[40] *Density Functional Theory of Time-Dependent Phenomena*, E.K.U. Gross, J.F. Dobson, and M. Petersilka, Topics in Current Chemisty, **181**, 81 (1996).

[41] *Many-Particle Physics*, G.D. Mahan, 2nd ed. (Plenum Press, New York, 1990).

[42] *Density-functional-theory response-property calculations with accurate exchange-correlation potentials* S.J.A. van Gisbergen, F. Kootstra, P.R.T. Shipper, O.V. Gritsenko, J.G. Snijders, and E.J. Baerends, Phys. Rev A. **57**, 2556 (1998)

[43] *Two electrons in an external oscillator potential: Particular analytic solutions of a Coulomb correlation problem*, M. Taut, Phys. Rev. A **48**, 3561 (1993).

[44] *Physics of transformation from Schrödinger theory to Kohn-Sham density-functional theory: Application to an exactly solvable model* Z. Qian and V. Sahni, Phys. Rev. A **57**, 2527 (1997)

[45] A. Yariv, *Quantum Electronics* (John Wiley & Sons, New York, 1988).

[46] M. Karplus and R. N. Porter *Atoms & Molecules* (Benjamin/Cummings, Menlo Park, California, 1970)

[47] W. Kinzel and G. Reents *Physics by Computer* (Springer, Berlin, 1998)

[48] G. Arfken *Mathematical methods for physicists* (Academic Press, New York, 1970)

[49] J. L. Powell, B. Crasemann *Quantum Mechanics* (Addison Wesley, 1961)

[50] S. Flügge *Practical Quantum Mechanics* (Springer)

[51] *Oscillator strengths for S-P and P-D transitions in heliumlike ions* N. M. Cann and A. J. Thakkar, Phys. Rev A. **46**, 5397 (1992)

[52] *Accurate oscillator strengths for neutral helium* A. Kono and S. Hattori, Phys. Rev. A **29**, 2981 (1984)

[53] *Calculation of thighter error bound for theoretical atomic-oscillator strengths* D. V. I. Roginsky, A. W. Weiss, Phys. Rev. A **38**, 1760 (1988)

[54] *Energy levels an the oscillator strengths of the Be atom determined by a configuration-interaction calculation with a finite basis set from B splines* T. N. Chang, Phys. Rev A **39**, 4946 (1988)

[55] C.J. Umrigar, private communication.

[56] *Exact high-density limit of correlation potential for two-electron density*, S. Ivanov, K. Burke, and M. Levy, J. Chem. Phys. **110**, 10262 (1999).

[57] *Comparison of exact and approximate density functionals for an exactly solvable model*, C. Filippi, C. J. Umrigar, and M. Taut, J. Chem. Phys. **100**, 1290 (1994).

[58] *Excitation energies from density functional perturbation theory*, C. Filippi, C.J. Umrigar, and X. Gonze, J. Chem. Phys., **107**, 9994 (1997).

[59] *Two electrons in an external oscillator potential: exact solution versus one-particle approximations* M. Taut, A. Ernst and H. Eschrig, J. Phys. B **31**, 2689 (1998)

[60] *Two electrons in an external oscillator potential: multiplet splittings from exact solutions and one-particle approximations* M. Taut and A. Ernst, J. Phys. B **31**, L35 (1998)

[61] S. Wolfram, Mathematica 3.0 (Wolfram Research 1988-96)

[62] *http://crab.rutgers.edu/~happel/thesis/*