

Documentationm for the RTA code in 3D

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Abstract

We present a RTA+TDLDA code on a cartesian 3D grid

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1. The subroutines in detail

SUBROUTINE `calc_Eref(occup, ispin, Ei, Eref)`

<code>occup(1:nstate)</code>	in	occupation number for s.p. states.
<code>ispin(1:nstate)</code>	in	spin assignement for s.p. states.
<code>Ei(1:nstate)</code>	in	spin assignement for s.p. states.
<code>Eref(1:2)</code>	out	sum of s.p. energies per spin.

Computes the weighted sum of s.p. energies as reference energy for DCMF. The sum is accumulated for each spin separately.

SUBROUTINE `fermi1(ekmod, eref, occup, ispinact, T0i, T1i, T2, mu)`

<code>ekmod(1:kstate)</code>	in	given s.p. energies, spin up block first, then spin down
<code>eref</code>	in	reference energy = wanted sum of s.p. energies
<code>ispinact</code>	in	spin for which routine is run
<code>T0i, T1i</code>	in	lower and upper temperature for search
<code>occup(1:kstate)</code>	in/out	occupation numbers, spin block-wise
<code>T2</code>	out	final temperature for which Fermi distribution matches <code>eref</code>
<code>mu</code>	out	final chemical potential

Determines thermal Fermi occupation such that given sum of s.p. energies `eref` and particle number is matched. Is done for each spin separately. Solution scheme is bracketing. Refers to SUBROUTINE `OccT1` while iterating temperature `T2`.

PGR2all: Nr. of spin-up/spin-down states comes through `m_params`. We should protocol all

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such entries. First step is to augment each **USE** by **ONLY** such that the explicitly communicated variables becomes visible.

PGR2all: Routine requires that arrays are sorted in continuous blocks of spin. Do we have an initial check for that?

```
SUBROUTINE OccT1(occrefloc,enerloc,Etotloc,muloc,occtotloc,n,T,occuploc)
    enerloc(1:n)    in    s.p. energies for actual spin
    n               in    number of s.p. states treated here
    T               in    temperature
    occrefloc       in    wanted total number of particles
    occuploc(1:n)   out   thermal occupation numbers for given T and s.p. energies
    muloc           out   chemical potential (Fermi energy)
    occtotloc       out   final total number of particles
    Etotloc         out   sum of s.p. energies
```

Determines by bracketing chemical potential **muloc** for given array of s.p. energies, temperature **T**, and wanted number of particles **occrefloc** with precision 1D-12. Delivers with it thermal occupation numbers and corresponding total particle number and sum of s.p. energies.

```
SUBROUTINE Calc_psi1(psi1,aloc,rhotot0,rhototloc,curr0,curr1,j,lambdaj,muj,sumvar2,eal)
combined with internal SUBROUTINE calc_hamiltonien.
    j               in    number of DCMF iteration, used here for print
    lambda(1:kdfull2,1:2) in    Lagrange parameter for density for spin up&down
    lambdaj(1:kdfull2,1:3) in    Lagrange parameter for current
    mu, muj         in    driving parameter for augmented Lagrangian
    aloc(1:2*kdfull2) in    local potentials for spin up and down
    rhotot0(1:kdfull2,1:2) in    initial density PGR2all: not used ??
    curr0(1:kdfull2,1:3) in    wanted current
    psi1(1:kdfull2,1:kstate) in/out set of s.p. wavefunctions iterated
    rhototloc(1:kdfull2,1:2) out    actual density according to psi1
    curr1(1:kdfull2,1:3) out    actual current from psi1
    ekmod(1:nstate) out    final s.p. energies
    eal             out    final sum of s.p. energies
    sumvar2         out    variance of s.p. energies
```

Performs one damped gradient step of with density & current constrained Hamiltonian.

PGR2all: The density array distinguishes spin up/down while the current array does not. Reason?

PGRcommThe IN & OUT assignments in this subroutine have to be updated.

```
SUBROUTINE eqstate(psi,aloc,rho,psi1,occuporth,iterat)
    iterat          in    actual iteration number (for printing)
    psi(1:kdfull2,1:kstate) in    initial set of s.p. wavefunctions
    psi1(1:kdfull2,1:kstate) out   final set of s.p. wavefunctions
    aloc(1:2*kdfull2) in/out    local part of potential, spin up/down stacked in blocks
    rho(1:2*kdfull2) in    initial density, spin up/down stacked in blocks
    occuporth(1:kstate) in    occupation numbers for psi and still the same for psi1.
```

DCMF iterations by repeatedly calling `Calc_psi1`, updating Lagrangian parameters for density & current constraints, and occasionally tuning temperature to achieve correct energy. The latter is done by calling `fermi1`. The local potential is kept constant during DCMF iteration and updated only at the very end.

PGR2all: Fetches `nr.` of spin up/down from `m.params`.

PGR2all: Lagrange parameters are started from scratch. May it be faster to recycle the previous Lagrange parameters?

PGR2all: Density `rho` is entered via list and still recomputed as `rho_tot0`. Unnecessary doubling?

2. Formula from Ann.Phys. paper

2.1. Mean-field propagation

The starting point and dominant feature of the dynamics is the propagation at the level of the mean field. In this paper, we are dealing with the electron dynamics in metal clusters and we describe it by time-dependent density functional theory at the level of the Time-Dependent Local-Density Approximation (TDLDA) treated in the real time domain [? ?]. It is augmented by a self-interaction correction (SIC) approximated by average-density SIC (ADSIC) [?] in order to attain correct ionization properties [?] in the course of the dynamical simulation. TDLDA is formulated within the usual Kohn-Sham picture in terms of a set of occupied single-particle (s.p.) wavefunctions $\{|\phi_\alpha\rangle, \alpha = 1 \dots N\}$. Their dynamics is described by the time-dependent Kohn-Sham equation

$$i\partial_t|\phi_\alpha\rangle = \hat{h}[\varrho]|\phi_\alpha\rangle \quad (1)$$

where \hat{h} is the Kohn-Sham mean-field Hamiltonian which is a functional of the instantaneous local density $\varrho(\mathbf{r}, t) = \sum_\alpha |\phi_\alpha(\mathbf{r}, t)|^2$ [? ?]. The time evolution delivered by Eq. (1) can be expressed formally by the unitary one-body time-evolution operator

$$\hat{U}(t, t') = \hat{\mathcal{T}} \exp \left(-i \int_{t'}^t \hat{h}(t'') dt'' \right) \quad (2a)$$

where $\hat{\mathcal{T}}$ is the time-ordering operator. This yields a closed expression for the time-evolution of s.p. states

$$|\phi_\alpha(t)\rangle = \hat{U}(t, t')|\phi_\alpha(t')\rangle. \quad (2b)$$

So far, TDLDA propagates pure states. Dissipation which we will add later on leads inevitably to mixed states. This requires to generalize the description from fully occupied s.p. wavefunctions to a one-body density operator $\hat{\rho}$. Its representation in configuration space, i.e. in terms of a given set of s.p. states $|\varphi_i\rangle$, reads in general $\hat{\rho} = \sum_{ij} |\varphi_i\rangle \rho_{ij} \langle \varphi_j|$. By appropriate transformation of the s.p. basis, one can diagonalize the density matrix ρ_{ij} which defines what are called natural orbitals. The natural orbitals representation of the one-body density operator then reads

$$\hat{\rho} = \sum_{\alpha=1}^{\infty} |\phi_\alpha\rangle W_\alpha \langle \phi_\alpha| \quad . \quad (3)$$

The weights W_α represent the probability with which a state $|\phi_\alpha\rangle$ is occupied. The mean-field propagation (1) then becomes

$$i\partial_t\hat{\rho} = [\hat{h}[\varrho], \hat{\rho}] \quad (4)$$

where $\hat{h}[\varrho]$ is formally the same as before and the local density is now computed as

$$\varrho(\mathbf{r}, t) = \sum_{\alpha} W_{\alpha} |\phi_{\alpha}(\mathbf{r}, t)|^2. \quad (5)$$

The (coherent) pure mean-field propagation (4) leaves the occupation weights W_α unchanged and propagates only the s.p. states. The mean-field propagation of an initial state (3) then reads

$$\hat{\rho}(t) = \sum_{\alpha=1}^{\infty} |\phi_{\alpha}(t)\rangle W_{\alpha} \langle\phi_{\alpha}(t)| = \hat{U}(t, 0)\hat{\rho}(0)\hat{U}^{-1}(t, 0) \quad (6)$$

where \hat{U} is the mean-field evolution operator (2a).

2.2. RTA in quantum-mechanical framework

The generalization of the one-body phase-space distribution $f(\mathbf{r}, \mathbf{p})$ to a quantum-mechanical mean-field theory is the one-body density operator $\hat{\rho}$, or one-body density matrix $\rho(\mathbf{r}, \mathbf{r}')$ respectively. The equation of motion for $\hat{\rho}$ including dynamical correlations reads in general [? ?]

$$i\partial_t\hat{\rho} - [\hat{h}, \hat{\rho}] = \hat{I}[\hat{\rho}] \quad (7)$$

The left hand side embraces the mean-field propagation. It may be time-dependent Hartree-Fock or the widely used LDA version of TDDFT. The right-hand side consists of the quantum-mechanical collision term. Motivated by the successful semi-classical RTA, we import Eq. (??) for the quantum case as

$$\partial_t\hat{\rho} = -i[\hat{h}, \hat{\rho}] - \frac{1}{\tau_{\text{relax}}} (\hat{\rho} - \hat{\rho}_{\text{eq}}[\varrho, \mathbf{j}, E]) \quad (8)$$

where $\hat{\rho}_{\text{eq}}$ is the density operator of the thermal equilibrium for local density $\varrho(\mathbf{r}, t)$, current distribution $\mathbf{j}(\mathbf{r}, t)$ and total energy $E(t)$ given at that instant of time t . These constraining conditions are, in fact, functionals of the actual state $\hat{\rho}$, i.e. $\varrho[\hat{\rho}]$, $\mathbf{j}[\hat{\rho}]$, and $E[\hat{\rho}]$. For the diagonal representation Eq.(3) of the density operator $\hat{\rho}$, they read

$$\varrho(\mathbf{r}) = \sum_{\alpha} |\phi_{\alpha}(\mathbf{r})|^2 W_{\alpha} \quad , \quad \mathbf{j}(\mathbf{r}) = \sum_{\alpha} W_{\alpha} \phi_{\alpha}^*(\mathbf{r}) \frac{\vec{\nabla} - \overleftarrow{\nabla}}{2i} \phi_{\alpha}(\mathbf{r}) \quad (9)$$

The energy $E(t)$ is taken as the total energy because the semi-classical concept of a local kinetic energy is ambiguous in a quantum system. This RTA equation (8) looks innocent, but is very involved because many entries depend in various ways on the actual state $\hat{\rho}(t)$. The self-consistent mean field is a functional of the actual local density, i.e.

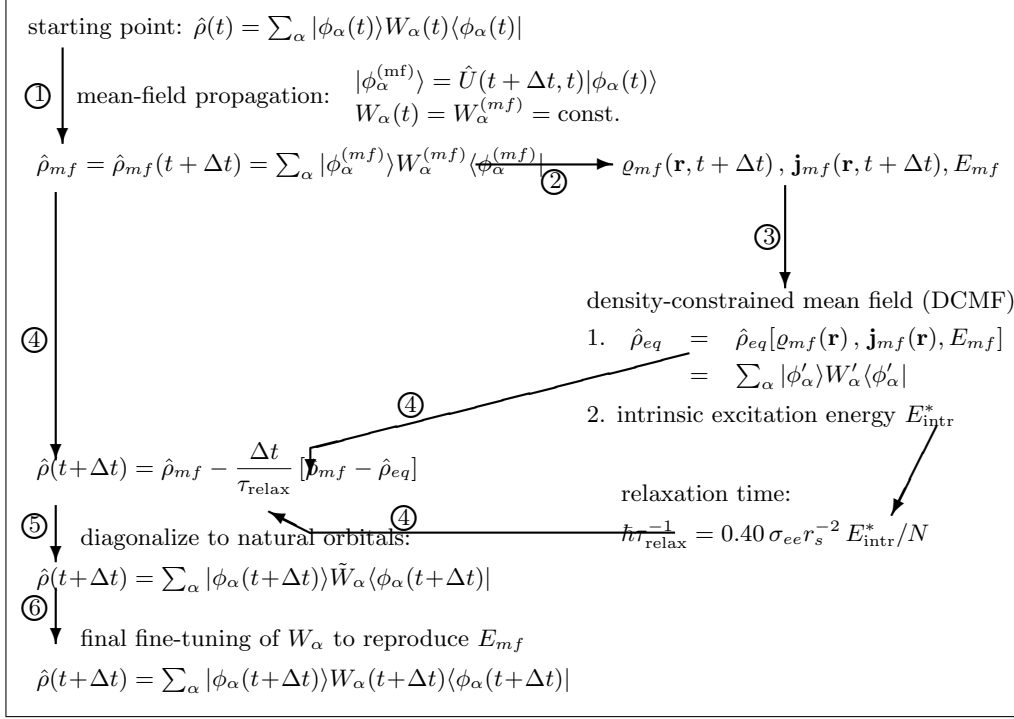


Figure 1: Sketch of the scheme for performing one large time step $t \rightarrow t + \Delta t$ in solving the RTA equations. The numbers in open circles indicate the steps as outlined in the text.

$\hat{h} = \hat{h}[\varrho]$. The instantaneous equilibrium density $\hat{\rho}_{eq}$ is the solution of the stationary, thermal mean-field equations with constraint on the actual $\varrho(\mathbf{r})$, $\mathbf{j}(\mathbf{r})$ and energy E , for details see Appendix ??.

The relaxation time τ_{relax} is estimated in semi-classical Fermi liquid theory, for details see appendix ??. For the metal clusters serving as test examples in the following, it becomes

$$\frac{\hbar}{\tau_{relax}} = 0.40 \frac{\sigma_{ee}}{r_s^2} \frac{E_{intr}^*}{N}, \quad (10)$$

where E_{intr}^* is the intrinsic (thermal) energy of the system (appendix ??), N the actual number of particles, σ_{ee} the in-medium electron-electron cross section, and r_s the effective Wigner-Seitz radius of the electron cloud. *Note that r_s is tuned to the average density of the electron cloud (appendix ??), because a spatially varying τ_{relax} would be very cumbersome to implement in a quantum mechanical context. This approximation is legitimate for metallic systems where the density remains generally close to the average.*

2.3. Summary of the procedure

The solution of the RTA equations is rather involved. We explain the necessary steps here from a practical side and unfold details in the appendices. We briefly summarize the actual scheme for one step from t to $t + \Delta t$. Note that mean-field propagation (actually

TDLDA) runs at a much faster pace than relaxation. We resolve it by standard techniques [? ?] on a time step δt which is much smaller (factor 10–100) than the RTA step Δt . We summarize this TDLDA propagation in the evolution operator \hat{U} from Eq. (2a) and discuss only one RTA step. Its sub-steps are sketched in Figure 1 and explained in the following whereby the label here correspond to the ones in the Figure:

1. We first propagate $\hat{\rho}$ by pure TDLDA. This means that the s.p. states in representation (3) evolve as $|\phi_\alpha(t)\rangle \rightarrow |\phi_\alpha^{(\text{mf})}\rangle = \hat{U}(t + \Delta t, t)|\phi_\alpha(t)\rangle$, while the occupation weights W_α are kept frozen (pure mean-field propagation).
2. We compute density $\varrho(\mathbf{r}, t + \Delta t)$, current $\mathbf{j}(\mathbf{r}, t + \Delta t)$, and total energy E_{mf} associated to the TDLDA-propagated density matrix $\hat{\rho}_{\text{mf}}$.
3. We determine the thermal mean-field equilibrium state $\hat{\rho}_{\text{eq}}$ constrained to the given ϱ , \mathbf{j} , and E_{mf} . This is achieved by Density-Constrained Mean Field (DCMF) iterations as outlined in Appendix ???. The actual equilibrium state $\hat{\rho}_{\text{eq}}$ is represented by new s.p. states $\{|\phi'_\alpha\rangle\}$ and new occupation numbers W'_α in diagonal form (3).
4. We compose the new density matrix from the TDLDA propagated state $\hat{\rho}_{\text{mf}}$ and the equilibration driving term $\hat{\rho}_{\text{mf}} - \hat{\rho}_{\text{eq}}$ with the appropriate weight $\Delta t/\tau_{\text{relax}}$, as outlined in Appendix ???. The relaxation time Eq. (10) requires the actual intrinsic excitation energy E_{intr}^* which is also obtained from DCMF, see appendix ??.
5. We diagonalize the state emerging from step 4 to natural-orbital representation Eq. (3). This yields the s.p. states $\{|\phi_\alpha(t + \Delta t)\rangle\}$ for the next step and preliminary new occupations \tilde{W}_α .
6. After all these steps, the initial energy $E_{\text{mf}} = E_{\text{TDLDA}}(t)$ may not be exactly reproduced. We may remain with a small energy mismatch as compared to the goal E_{mf} . We now apply a small iterative thermalization step to readjust the energy, as outlined in Appendix ???. This then yields the final occupation weights $W_\alpha(t + \Delta t)$ which comply with energy conservation.

The scheme can be used also in connection with absorbing boundary conditions [? ?]. The particle loss will be mapped automatically to loss of occupation weights in step 4. A word is in order about the choice of the time steps. The δt for propagation of TDLDA is limited by the maximal energy on the grid representation and thus very small (for Na clusters typically 0.005 fs). The stepping for the relaxation term needs only to resolve the changes in the actual mean field which is achieved already with $\Delta t \approx 0.5$ fs. We have tested a sequence of Δt and find the same results for all $\Delta t \leq 0.5$ fs. Changes appear slowly above that value. For reasons of efficiency, we thus use the largest safe value of $\Delta t = 0.5$ fs.

A word is in order about the range of applicability of the RTA for finite fermion systems. The relaxation time τ_{relax} is allowed to depend on time which allows to accommodate changes of the dynamical state. But τ_{relax} is at each instant if time one global number chosen according to the average electron density. This requires systems with only small density variations in the bulk as it holds typically for metallic bonds. The RTA is insensitive to many details of the VUU collision term as energy- and angle-dependent scattering cross sections or a broad spectrum of relaxation rates. However, these details are usually resolved only (if at all) for fast and energetic processes which are anyway deep in the regime of semi-classical VUU. The grossly averaged treatment of RTA is acceptable for not too fast and not too energetic processes in compact metallic systems.

2.4. Numerical representation and computation of relevant observables

The numerical implementation of TDLDA is done in standard manner [? ?]. The coupling to the ions is mediated by soft local pseudopotentials [?]. The Kohn-Sham potential is handled in the Cylindrically Averaged Pseudo-potential Scheme (CAPS) [? ?], which has proven to be an efficient and reliable approximation for metal clusters close to axial symmetry. Wavefunctions and fields are thus represented on a 2D cylindrical grid in coordinate space [?]. For the typical example of the Na₄₀ cluster, the numerical box extends up to 104 a₀ in radial direction and 208 a₀ along the z -axis, while the grid spacing is 0.8 a₀. To solve the (time-dependent) Kohn-Sham equations (1) we use time-splitting for time propagation [?] and accelerated gradient iterations for the stationary solution [?]. The Coulomb field is computed with successive over-relaxation [?]. We use absorbing boundary conditions [? ?], which gently absorb all outgoing electron flow reaching the bounds of the grid and thus prevent artifacts from reflection back into the reaction zone. We take the exchange-correlation energy functional from Perdew and Wang [?].

A great manifold of observables can be deduced from the $\hat{\rho}(t)$ thus obtained. We will consider in the following the dipole signal, dipole spectrum, ionization, angular distribution of emitted electrons, and entropy. We focus here on the dipole moment along symmetry axis z , which is obtained from the local density as $\langle \hat{d}_z \rangle(t) = \int d^3r d_z(z) \varrho(r)$ where $d_z(z) = z$ is the (local) dipole operator. The dipole strength distribution is computed with the methods of spectral analysis [?]. It is attained by an instantaneous dipole-boost excitation, collecting $\langle \hat{d}_z \rangle(t)$ during propagation, and finally Fourier transforming $\langle \hat{d}_z \rangle(t)$ into frequency domain. The angular distribution of emitted electrons is obtained from recording the absorbed electrons as in TDLDA [? ?]. The angular distribution is characterized by the anisotropy parameter β_2 , the leading parameter in the photo-electron angular cross section $d\sigma/d\Omega \propto (1 + \beta_2 P_2(\cos(\theta)) + \dots)$ [? ?] where P_2 is the second order Legendre polynomial and θ the direction with respect to laser polarization axis (here z -axis in 2D cylindrical geometry). A specific quantity to track relaxation processes is the one-body entropy which is computed in diagonal representation (3) by the standard expression [?]

$$S = - \sum_{\alpha} [W_{\alpha} \log W_{\alpha} + (1 - W_{\alpha}) \log(1 - W_{\alpha})] \quad (11)$$

in units of Boltzmann constant. It serves as a direct indicator of thermalization and allows to read off the typical time scale of relaxation processes.