Time-Dependent Density-Functional Theory (TD-DFT): A Hands-On Tutorial^{*}

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Abstract

This text was prepared for the DEMON2K and DEMON-NANO tutorial which took place from 15 to 20 June 2015 at the CECAM center in the IDRIS supercomputing center in Orsay, near Paris, France. After beginning with a brief review of the theory, we rapidly go into the history of time-dependent (TD) density-functional theory (DFT) in the DEMON programs. This helps to give an idea of the historical place of DEMON in the development of TD-DFT in quantum chemistry and physics, its current position, and some idea of what is to come. This historical part is then followed by specific example calculations to be run by the students in DEMON2K version **4.3.2** in order to improve their understanding of TD-DFT. Finally we end with a section on keywords in different versions of the DEMON programs.

PACS numbers: Valid PACS appear here Keywords: Davidson

 $^{^{\}ast}$ for the DEMON2K tutorial at Paris

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I. INTRODUCTION

Time-dependent (TD) density-functional theory (DFT) may be viewed as an extension of ordinary time-independent ground stationary state Hohenberg-Kohn-Sham DFT into the time domain. Information about electronic excited states may be obtained by linear response (LR) theory and, in fact, the calculation of electronic absorption spectra by LR-TD-DFT is the most common application of TD-DFT. We will focus here on learning to run LR-TD-DFT calculations in the DEMON program. But first we must give the reader a bit of background.

TD-DFT is based upon two theorems. To understand these theorems, imagine that our system is initially in its ground stationary state so that traditional Hohenburg-Kohn-Sham DFT applies. Now turn on a time-dependent electric field. Then, modulo certain assumptions, Runge and Gross proved that the time-dependent external field is determined up to a function of time by the time-dependent charge density:

$$\rho(\vec{r}t) \to v_s(\vec{r}t) + C(t). \tag{1}$$

This means that the time-dependent charge density determines the wave function up to a time-dependent phase factor,

$$\rho(\vec{r}t) \to \Psi(t)e^{i\int C(t)dt} \,. \tag{2}$$

The second theorem, which is also subject to certain assumptions, states that there is a time-dependent noninteracting system of electrons with the same charge density as the real interacting system [33]. Thus there is a TD Kohn-Sham equation,

$$\left[\hat{h}_{H} + v_{xc}[\rho](\mathbf{r}t)\right]\psi_{i}(\mathbf{r}t) = i\frac{\partial}{\partial t}\psi_{i}(\mathbf{r}t), \qquad (3)$$

where v_{xc} is the TD exchange-correlation (xc) potential. Although these theorems have only been proven within the limits of certain assumptions, on-going work is aimed at reducing the severity of these assumptions. It is generally felt that TD-DFT has a fairly firm formal foundation and it certainly widely used for many practical applications. Most practical approximations are based upon the TD-DFT adiabatic approximation,

$$v_{xc}[\rho](\vec{r}t) \approx v_{xc}[\rho_t](\vec{r}), \qquad (4)$$

which assumes that the xc-potential reacts instantaneously and without memory to any temporal change of the charge density. Here v_{xc} is the functional derivative with respect to the xc energy of traditional Hohenburg-Kohn-Sham DFT and $\rho_t(\vec{r})$ is $\rho(\vec{r}t)$ evaluated at the time t. More information may be found in recent books [7, 9, 18] and review articles [3, 6, 11, 12, 20].

Excitation energies and oscillator strengths may be found by solving Casida's RPA-like formulation of LR-TD-DFT [38]. The result is the matrix equation,

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{bmatrix} \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix} = \omega \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ -\mathbf{1} & \mathbf{0} \end{bmatrix} \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix},$$
(5)

where, including spin,

$$A_{ia,jb}^{\sigma,\tau} = \delta_{\sigma,\tau} \delta_{i,j} \delta_{a,b} (\epsilon_a - \epsilon_i) + (ai|f_H|jb) + (ai|f_{xc}^{\sigma,\tau}|jb) , \qquad (6)$$

and,

$$B_{ia,bj} = -(ia|f_H|jb) + (ia|f_{xc}^{\sigma,\tau}|jb), \qquad (7)$$

where, in the adiabatic approximation,

$$f_{xc}^{\sigma,\tau}(\vec{r}_1, \vec{r}_2; t_2 - t_1) = \delta(t_2 - t_1) \frac{\delta^2 E_{xc}}{\delta \rho_{t_1}^{\sigma}(\vec{r}_1) \delta \rho_{t_2}^{\tau}(\vec{r}_2)} \,. \tag{8}$$

The excitation energy,

$$E_I - E_0 = \hbar \omega_I \,, \tag{9}$$

while the oscillator strength (which is the intensity of the absorption in a stick spectrum) is the unitless quantity,

$$f_I = \frac{2\omega_I m_e}{3\hbar} |\langle \Psi_0 | \vec{r} |^2 \,. \tag{10}$$

calculated from the vectors \vec{X} and \vec{Y} . In the limit of a complete basis set, the oscillator strengths satisfy the TRK *f*-sum rule,

$$\sum_{I} f_{I} = N \,, \tag{11}$$

where N is the total number of electrons in the system.

The LR-TD-DFT equation above is sometimes solved in the Tamm-Dancoff approximation (TDA) [32] in which $\mathbf{B} = \mathbf{O}$,

$$\mathbf{A}\vec{X} = \omega\vec{X} \,. \tag{12}$$

Although this looks, at first glance, like an approximation, it is sometimes an improvement. Thus although LR-TD-HF obeys the TRK f-sum rule, it is not variational. The TDA LR-TD-HF is the same as CIS. The f-sum rule is lost, but a variational theory is obtained which is sometimes useful, especially for photochemical applications [14].

A. Casida's Equations

II. PROGRAMS

As this document concerns using TD-DFT in the DEMON suite of programs, we must start by saying a little about these programs. Thus we start with a brief history of DEMON and then continue with a brief description of the principle versions implementing TD-DFT—namely, DEMON-DYNARHO, DEMON2K, DE-MON2K@GRENOBLE, and a brief preview of work in progress which may be expected in future versions. DEMON is short for *densité de Montréal* ("density of Montreal.") It is a family of programs which grew out of Alain St-Amant's PhD thesis with Dennis R. Salahub at the *Université de Montréal* (UdM) in Montreal, Quebec, Canada. The main DEMON program of that period came to be known as DEMON-KS for deMon Kohn-Sham.

Beginning around 1995, the master DEMON program began to be rewritten from the bottom up. The principal author of the current master version of DEMON, known as DEMON2K, is Andreas Kster. The official citation for that version is,

DEMON2K, Andreas M. Köster, Patrizia Calaminici, Mark E. Casida, Roberto Flores-Moreno, Gerald Geudtner, Annick Goursot, Thomas Heine, Andrei Ipatov, Florian Janetzko, Jorge M. del Campo, Serguei Patchkovskii, J. Ulises Reveles, Dennis R. Salahub, Alberto Vela, The International deMon Developers Community (Cinvestav-IPN, Mexico, 2006).

Gerald Geudtner is currently responsible for gathering updates from DEMON developers and putting them in this master version.

However there are several associated programs and evolutionary spin-offs of DE-MON2K and of the earlier DEMON-KS. One such is the Stockholm-Berlin (STOBE) version of DEMON-KS. Another is the DEMON2K-KSCED spin-off of DEMON2K, developed in Geneva in Tomasz Wesołowski's group, which allows for two types of beyond-Kohn-Sham methods: (i) orbital-free embedding calculations following Wesolowski-Warshel embedding formalism, and (ii) fully variational calculations following Cortona formulation of density functional theory. In Grenoble, we also have our own local development version of DEMON2K which we call DEMON@GRENOBLE. An important predecessor of DEMON@GRENOBLE was DEMON-DYNARHO.

It is a bit hard to define what exactly makes DEMON so special. Is it the people who haved worked on it over the years? The innovative things we have done with the program which have since spread to other quantum chemistry and physics programs? Suffice it to say that most DEMON programs are characterized by the use of a double basis set. The molecular orbitals are expanded in an orbital basis set consisting of atomic orbitals represented as contractions of Gaussian-type orbitals,

$$\psi_i(\vec{r}) = \sum_{\mu} (\vec{r}) c_{\mu,i} \,. \tag{13}$$

The density,

$$\rho(\vec{r}) = \sum_{i} \psi_{i}(\vec{r}) n_{i} \psi_{i}^{*}(\vec{r})
= \sum_{\mu,\nu} \chi_{\mu}(\vec{r}) \left(\sum_{i} c_{\mu,i} n_{i} c_{\nu,i}^{*} \right) \chi_{\nu}^{*}(\vec{r})
= \sum_{\mu,\nu} \chi_{\nu}(\vec{r}) \chi_{\nu}^{*}(\vec{r}),$$
(14)

is approximated by an expansion in an auxiliary basis set,

$$\tilde{\rho}(\vec{r}) = \sum_{I} f_{I}(\vec{r}) a_{I} , \qquad (15)$$

where the fitting coefficients are obtained by minimizing the electron repulsion "error" integral,

$$||\Delta\rho||^{2} = [\rho - \tilde{\rho}|\frac{1}{r_{12}}|\rho - \tilde{\rho}].$$
(16)

This auxiliary basis allows all 4-center electron repulsion integrals to be eliminated from deMon, thus permitting a formal $\mathcal{O}(N^3)$ scaling, instead of the usual formal $\mathcal{O}(N^4)$ (or worse) scaling of normal *ab initio* quantum chemistry programs. In practice scaling can be significantly better than $\mathcal{O}(N^3)$ because of additional tricks of the trade. Another program with a similar philosphy was DGAUSS, developped at Cray Inc. Of course, there is much more to DEMON programs than just auxiliary basis sets, but that and analytic derivatives for geometry optimizations was a key historical starting point for DEMON. The official DEMON site is

http://www.demon-software.com/public_html/index.html .

A. DEMON-DYNARHO

The post DEMON-KS program, DEMON-DYNARHO is the immediate predecessor of Grenoble's contributions to DEMON2K. It represents what was probably the first implementation of LR-TD-DFT in a Quantum Chemistry program. (Notes in French and in English for an introductory course on TD-DFT may be found at

https://sites.google.com/site/markcasida/tddft .)

A detailed account of what are sometimes known as "Casida's equation" for linear response theory is given in Ref. [38]. The approach described therein was implemented in DEMON-DYNARHO [37, 39]. We used DEMON-DYNARHO to make several contributions to the scientific community. These include a highly-cited article [35] on the artificially low onset of the TD-DFT ionization threshold at $-\epsilon_{HOMO}$, as well as articles [29, 34] reporting a simple asymptotic correction scheme to fix the problem. Article [35] is also interesting in so far as it represents the first treatment of an avoided crossing within a DFT-based method. An attempt was made to reconcile TD-DFT with the Δ SCF method which often gives similar results when both are applicable [28, 31]. The spectra of open-shell molecules has been investigated [30]. The Optimized Effective Potential (OEP) method was treated in the context of the resolution-of-the-identity (RI) approximation to exchange [25–27]. We also used DEMON-DYNARHO to make some contributions to the problem of DFT-based calculations of NMR chemical shifts [22–24].

In short, we made a significant number of contributions to DFT and TD-DFT using DEMON-DYNARHO. The citation of one of the last official versions of this program was,

DEMON-DYNARHO version 3.1, M.E. Casida, C. Jamorski, J. Guan, S. Hamel, and D.R. Salahub, University of Montreal, 2001.

Note that DEMON-DYNARHO was never intended to be much more than a prototype "toy" program to investigate fundamental aspects of TD-DFT on very simple systems. We learned a lot from this program and it became stable and reliable for calculations on small molecules, but we could not handle even moderately large systems such as p-nitroaminobenzene. And the post-SCF nature of DEMON-DYNARHO prevented us from implemented excited-state forces.

B. Current Master Version of DEMON2K

Around 2001, a decision was made to integrate TD-DFT (and other good features) from DEMON-DYNARHO into the master version of DEMON2K [17]. This was aided by Franco-Mexican ECOS financing for a joint project. Mark E. Casida and his first French doctoral student Anthony Fouqueau both traveled to Mexico and were instrumental in the integration. Perhaps even more critically was the presence of a Russian postdoc, Andrei Ipatov, in Grenoble who was able to make even more progress on the integration and whose name figures on the author list for DEMON2K). The results was a success in that we can now routinely handle larger molecules than DEMON-DYNARHO ever could.

C. DEMON2K@GRENOBLE

But we still lack in DEMON2K many features from DEMON-KS/DEMON-DYNARHO which we are gradually putting into our local development version, EMON2K@GRENOBLE. At the same time, we are using DEMON2K@GRENOBLE to test out new creative ideas.

Grenoble developments which may find their way into future versions of DE-MON2 κ include: (1) Calculation of the expectation value of S^2 for excited states in TD-DFT[16] and (2) noncollinear spin-flip TD-DFT [10]. We are also working on (1) improving the block Davidson procedure, (2) analytic derivatives for TDDFT excited states, (3) polarization propagator corrections going beyond the TD-DFT adiabatic approximation [1, 8], and (4) TD-DFT with fractional occupation numbers.

D. TD-Auxiliary Function DFT

A particularly strong point of the DEMON programs is the use of auxiliary fitting functions. Recently new ways have been developed in Mexico in order to carryout time-dependent response theory in such a way as to take additional explicit advantage of these auxiliary functions in a parallized code [4] [5] [2]. One "difficulty" that we are going to have to face is how to make the correspondance between this TD-auxiliary function DFT (TD-ADFT) and Casida's equations which have also been developed using auxiliary fitting functions. We should be able to expect these two approaches to merge in future versions of DEMON2K.

III. HANDS-ON EXAMPLES

A. Job Submission

We will run on the Idris computers using the same commands that you learned during the first hands-on session on Tuesday. Alternatively you may run DEMON2K on yourown machine.

B. \mathbf{H}_2

Diatomic hydrogen (H_2) is the world's simplest molecule (unless we consider H_2^+ !) We will first use H_2 as we learn to crawl and then we will go further with other molecules as we learn to walk.

We have learned that the basic ground- and excited-state wave functions are not often as well understood as they should be. So please have a look at the following document before you start:

3rd Year Chemistry, Advanced Chemical Physics: Qualitative Quantum Chemistry, Exercises assigned by Mark E. CASIDA Lesson 1: Study of the H2 Moleculej, January 27, 2015

This is a document (translated into English) which is part of an optional third year course on advanced chemical physics (that I teach in French).

1. Minimal basis set calculations

Let us do a minimal basis set (STO-3G) basis set calculation at a geometry close to the experimental geometry. The experimental bond length of H₂ is R = 0.741 Å or R = 1.40 bohr (1 bohr = 0.529177249 Å). This is such a simple example that you should be able to anticipate many of your results before you get them. Remember what Louis Pasteur said,

"Chance favors the prepared mind."

Put another way, you are more likely to be surprised, and so to learn something, if you first try to anticipate your results and then carefully verify whether your ideas correspond or not to what you actually found.

- 1. Exercise 1 is just to draw the molecular orbital (MO) diagram as best you can as you learned it in your early chemistry courses. Also try to anticipate what the excited-states should be: How many should there be? Of what type?
- 2. Now run the TD-DFT calculation with the LDA functional (TDLDA) with the following input file:

```
TITLE H2: (H2) (Basis: GEN-A3*/STO-3G)
MULTI 1
#
SCFTYP RKS TOL=0.1E-07
```

```
GRID FIXED FINE
MIXING 0.1
#
VXCTYPE VWN
#
EXCITATION DAVIDSON
DAVIDSON BAS=30 EIG=25
#
PRINT MOS
VISUALIZATION MOLDEN FULL
POPULATION
#
# --- GEOMETRY ---
# deMon2k : VWN/GEN-A3*/3-21G opt
#
GEOMETRY Z-MATRIX BOHR
Η
H 1 R1
#
VARIABLES
R1 1.45165175
#
# --- BASIS (GEN-A3*/STO-3G) ---
#
AUXIS (GEN-A3*)
BASIS
H READ
1 0 3
3.42525091 0.15432897
0.62391373 0.53532814
0.16885540 0.44463454
#
```

Here the basis has been entered explicitly. The STO-3G basis set consists of a single 1s orbital on each hydrogen atom made up of a contracted linear combination of three gaussian functions. The exponents of the gaussian functions (3.42, 0.624, 0.169) are on the left and the contraction coefficients (0.154,0.535,0.445). However

BASIS (STO-3G)

should also work just as well as the STO-3G basis is in the BASIS file.

- 3. Hopefully the job ran correctly. The SCF converged and the TD-DFT part finished correctly. Have a good look at the output. Do you find the excited states that you expected to find? There are also some new things: What is $\langle \hat{S}^2 \rangle$? What are the oscillator strengths and why should you expect them to be the way they are? Also what are the "STRENGTH FUNCTION MOMENTS"?
- 4. Now let us repeat the same calculation but really stretch the bond so that R = 3.65 Å. Can you guess what will happen? Here is the input to use:

```
TITLE H2 (SPE): (H2) (Basis: GEN-A3*/STO-3G)
MULTI 1
#
SCFTYP RKS TOL=0.1E-07
GRID FIXED FINE
MIXING 0.1
#
VXCTYPE VWN
#
EXCITATION DAVIDSON
DAVIDSON BAS=30 EIG=25
#
PRINT MOS
VISUALIZATION MOLDEN FULL
POPULATION
#
# --- GEOMETRY ---
# deMon2k : VWN/GEN-A3*/3-21G opt
#
GEOMETRY Z-MATRIX BOHR
Η
H 1 R1
#
VARIABLES
R1 3.65
#
# --- BASIS (GEN-A3*/STO-3G) ---
#
AUXIS (GEN-A3*)
```

```
BASIS
H READ
1 0 3
3.42525091 0.15432897
0.62391373 0.53532814
0.16885540 0.44463454
#
```

5. Compare the result with the same calculation made with the Tamm-Dancoff approximation (TDA).

```
TITLE H2 (SPE): (H2) (Basis: GEN-A3*/STO-3G)
MULTI 1
#
SCFTYP RKS TOL=0.1E-07
GRID FIXED FINE
MIXING 0.1
#
VXCTYPE VWN
#
EXCITATION DAVIDSON TDA
DAVIDSON BAS=30 EIG=25
#
PRINT MOS
VISUALIZATION MOLDEN FULL
POPULATION
#
# --- GEOMETRY ---
# deMon2k : VWN/GEN-A3*/3-21G opt
#
GEOMETRY Z-MATRIX BOHR
Η
H 1 R1
#
VARIABLES
R1 3.65
#
# --- BASIS (GEN-A3*/STO-3G) ---
#
AUXIS (GEN-A3*)
```

```
BASIS
H READ
1 0 3
3.42525091 0.15432897
0.62391373 0.53532814
0.16885540 0.44463454
#
```

What has changed?

6. Normally the full TDLDA response calculation and the TDA TDLDA response calculation give nearly the same excitation energies near the equilibrium bond length. Please check:

```
TITLE H2: (H2) (Basis: GEN-A3*/STO-3G)
MULTI 1
#
SCFTYP RKS TOL=0.1E-07
GRID FIXED FINE
MIXING 0.1
#
VXCTYPE VWN
#
EXCITATION DAVIDSON TDA
DAVIDSON BAS=30 EIG=25
#
PRINT MOS
VISUALIZATION MOLDEN FULL
POPULATION
#
# --- GEOMETRY ---
# deMon2k : VWN/GEN-A3*/3-21G opt
#
GEOMETRY Z-MATRIX BOHR
Η
H 1 R1
#
VARIABLES
R1 1.45165175
#
```

```
# --- BASIS (GEN-A3*/STO-3G) ---
#
AUXIS (GEN-A3*)
BASIS
H READ
1 0 3
3.42525091 0.15432897
0.62391373 0.53532814
0.16885540 0.44463454
#
```

2. Large basis set calculation

Now let us do a reality check! We will do a calculation for H_2 near the equilibrium geometry with the Sadlej basis set. The Sadlej basis set was originally developed for calculating polarizabilities and hyperpolarizabilities with wave function correlated methods. It might be called a "medium-sized" basis set for wave function methods but it is a bit on the large size for many DFT applications.

1. Run the calculation with the input file:

```
TITLE H2 : (H2) (Basis: GEN-A3*/SAD)
MULTI 1
#
SCFTYP RKS TOL=0.1E-07
GRID FIXED FINE
MIXING 0.1
#
VXCTYPE VWN
#
EXCITATION DAVIDSON
DAVIDSON BAS=30 EIG=25
#
PRINT MOS
VISUALIZATION MOLDEN FULL
POPULATION
#
# --- GEOMETRY ---
# deMon2k : VWN/GEN-A3*/3-21G opt
```

```
#
GEOMETRY Z-MATRIX BOHR
H
H 1 R1
#
VARIABLES
R1 1.45165175
#
# ---- BASIS (GEN-A3*/STO-3G) ----
#
AUXIS (GEN-A3*)
BASIS (SAD)
#
```

- 2. Verify that the SCF has converged. Examine the MO coefficients and assign the orbital symmetries (σ_g , σ_u , π_g , π_u). Make a table of MO symmetries to help you understand your excitation energy results.
- 3. For the first time, the response matrix is large enough that you are able to see the block Davidson diagonalization in action. Can you find the relevant part of the output? This happens to be a case where near linear dependencies creep into the calculation so that some of the results are artifacts rather than being physical. Can you identify and separate the nonphysical results that you should throw out from the ones you should keep? (Note that this is not just something you see in DEMON2K but also in many other programs.)
- 4. Assign your excited state symmetries and explain why certain states have zero oscillator strengths and others nonzero oscillator strengths.
- 5. Now go to the NIST web book and compare with real experimental data:

http://webbook.nist.gov/cgi/cbook.cgi?ID=C1333740&Units=SI&Mask=1000#Diatomic

Why should you are should you not expect agreement between your calculations and the experimental values?

State	Experimental Excitation Energy (eV)
$C^{3}\Pi_{u}$	11.19
$w {}^1\Delta_u$	10.27
$a' {}^1\Sigma_u^-$	9.92
$B' {}^{3}\Sigma_{u}^{-}$	9.67
$a {}^{1}\Pi_{g}$	9.31
$W^{3}\Delta_{u}$	8.88
$B{}^{3}\Pi_{g}$	8.04
$A^{3}\Sigma_{u}^{+}$	7.75

TABLE I. Experimental Excitation Energies of N_2 at a bond length of 1.0977 Å.

C. N_2

You have learned quite a bit from your little calcualtions on H_2 . Now let us look at a system which is still small but more interesting, namely N_2 . In their seminal paper Jamorski *et al.* carried out TD-DFT calculations [37] and compared against the following experimental values (Table I). Carry out and analyze the calculation with the following input:

```
# -----
TITLE N2: (N2) (Basis: GEN-A3*/Sadlej)
MULTI 1
#
SCFTYP RKS TOL=0.1E-07
GRID FIXED FINE
#
VXCTYPE VWN
#
EXCITATION DAVIDSON
DAVIDSON BAS=46 EIG=46
#
PRINT MOS
VISUALIZATION MOLDEN FULL
POPULATION
#
# --- GEOMETRY ---
# Ground-state expt. equilibrium internuclear dist. R=1.0977A
# "K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure.
```

Make a table comparing the experimental and calculated excitation energies. Do you notice anything peculiar about the first states? What about states 8 and 9? Is there anything here that should set off alarm bells for a thoughtful theoretician? Also where do you think the ionization continuum starts in this calculation?

D. Oxirane H_2COCH_2

As a final, slightly more challenging calculation, let us calculate the spectrum of oxirane and compare with the spectrum given at the NIST site:

```
http://webbook.nist.gov/cgi/cbook.cgi?ID=C75218&Units=SI
```

(You must click on "UV/Visible spectrum".) Use the input file:

```
# -----
TITLE Oxirane: (C2H4O) (Basis: GEN-A3*/SAD)
# ethylene oxide
MULTI 1
#
SCFTYP UKS TOL=0.1E-07
GRID FIXED FINE
#
VXCTYPE VWN
#
EXCITATION DAVIDSON
DAVIDSON BAS=30 EIG=20
#
PRINT MOS
VISUALIZATION MOLDEN FULL
POPULATION
#
# --- GEOMETRY ---
# From: https://sites.google.com/site/markcasida/tddft
#
GEOMETRY CARTESIAN ANGSTROM
C1 5.7160010 4.6975500 4.4702530
C2 4.2685420 4.8618660 4.6851930
   5.0599580 5.5794390 5.6592610
0
H1 6.3948730 5.2549090 4.0177590
H2 3.5708170 4.0749812 5.0613610
H3 6.1242200 3.8003140 5.1425900
H4 3.8995360 5.5309330 3.9226910
#
# --- BASIS (GEN-A3*/6-311++G**) ---
#
AUXIS (GEN-A3*)
```

BASIS (SAD) # # -----

You may calculate the molar absorptivity spectrum using spectrum_plus.py from

https://sites.google.com/site/markcasida/tddft

(Go down to the bottom of the page.)

IV. KEYWORDS

A. DEMON-DYNARHO

The main purpose here is to show you how far the capabilities of the original program had evolved.

The preliminary input is followed by the main input, described here one by one. The minimum amount of input is indicated using capital letters, while small letters indicate the rest of the keyword. When one or more options are possible for a given keyword, they are indicated as choices within parentheses.

1. MODULE RESPONSE

This is always the first line of the input file.

2. EXCItation (FULL, DAVIdson nwant rcutoff limit maxiter)

The EXCItation keyword requests the calculation of the excitation spectrum. The default is not to calculate the spectrum. The option FULL means to set up and diagonalize the full response theory problem. This is possible for only the smallest molecules. The option DAVIdson allows larger molecules to be treated by using the block Davidson algorithm for finding the lowest eigenvalues and eigenvectors of a large matrix (without actually creating and storing the large matrix). The DAVIdson keyword must be followed by the four numbers "nwant rcutoff limit maxiter," where

- **nwant** is (half) the number of guesses which the block Davidson method will try to converge.
- **rcutoff** is the convergence criterion (in eV) for the excitation energies.
- **limit** is the dimension of the largest matrices which should be diagonalized.

- **maxiter** is the maximum number of Davidson iterations to be allowed. BE CAREFUL: There are no defaults for these four numbers!
- 3. INTEgrals (MO, AO) (ACTIve minorb maxorb) Form the coupling matrix or its action on a vector by either an AO-based or MO-based algorithm. The default is MO. The ACTIve keyword is optional and restricts calculations to a subspace of active molecular orbitals. Here
 - minorb is the number of the smallest active orbital.
 - **maxorb** is the number of the largest active orbital.
- 4. **POLArizability (STATic, DYNAmic)** The POLArizability key word requests the calculation of the dipole polarizability by matrix inversion. The default is not to do the calculation. Either STATic or DYNAmic polarizabilities may be calculated. PREScreening THR1 THR2 This sets a threshold of 10**(-THR1) for local prescreening in the calculation of the overlap and exchange-correlation second-derivative matrices in the auxiliary basis representation, and a threshold of 10**(-THR2) for global prescreening used in the construction of the exchange-correlation B matrices. The default is THR1=8 and THR2=8. For more information and test results click here.
- 5. SCF (LDA, HF, OEP, KLI) (FIRST, (MAXSCF, ENCONV, DMIX)) The SCF keyword specifies deMon-DynaRho should carry out the self-consistent field calculation which preceeds the response theory calculation, instead of just taking the result directly from deMon-KS. The choices of SCF calculation in **DynaRho** are:
 - LDA local density approximation
 - $\bullet~{\rm HF}$ Hartree-Fock
 - OEP exchange-only optimized effective potential
 - KLI pseudo Krieger-Li-Iafrate (i.e. the average denominator approximation is made in the OEP calculation)

All of these are done in the resolution-of-the-identity (RI) approximation. These keywords need to be followed by either:

- FIRST first-order calculation only (i.e. single iteration)
- (MAXSCF,ENCONV,DMIX) iterate with a mixing of DMIX until an total energy change of ENCONV for eight consecutive iterations for a maximum of MAXSCF iterations

- 6. LEVEl (IPA, RPA, XA, LDA) The LEVEl keyword specifies the level of calculation of the TD-DFRT coupling matrix. Here, IPA denotes the independent particle approximation, RPA denotes the density-functional theory random phase approximation, XA denotes the time-dependent X alpha method with alpha=2/3, while LDA denotes the full time-dependent local density approximation (TDLDA).
- 7. **TWOLevel (NMR)** For closed-shell TDLDAxc calculations, this calculates the singlet and triplet TDLDA and DeltaSCF energies in the twolevel model described in Ref. [C96]. If the NMR option is used, then an NMR input file will be created for a modified version of the chemical shift part of deMon-NMR.
- 8. **SPINblocking (SINGlet, TRIPlet, BOTH, NONE)** Explicitly block the TDDFT Omega matrix according to spin-coupling.
 - **SINGlet** Calculate singlet-coupled results only.
 - **TRIPlet** Calculate triplet-coupled results only.
 - **BOTH** The default. Calculate both singlet- and triplet-coupled results.
 - NONE Do not block according to spin-coupling.
- 9. **PROPERTY DIPOLE** This line is mandatory.
- 10. **END** This is always the last line.
- **B.** DEMON2K

The Master version of DEMON2K has an on-line manual at

http://www.demon-software.com/public_html/support/htmlug/index.html

The relevant part for us is:

Keyword **EXCITATION**

This keyword specifies a time-dependent DFT (TDDFT) calculation.

Options:

DAVIDSON / RS / DSYEV / D&C / JACOBI

DAVIDSON Iterative Davidson diagonalization of TDDFT matrix.

- **RS** EISPACK Householder diagonalization of TDDFT matrix. This is the default.
- **DSYEV** LAPACK Householder diagonalization of TDDFT matrix.
- **D&C** LAPACK divide and conquer diagonalization of TDDFT matrix.
- **JACOBI** Jacobi diagonalization of TDDFT matrix.
- **TDA** Activation of Tamm-Dancoff approximation.

Description:

Excitation energies and oscillator strength are calculated using the formulation of Ref. [37] [17] [16]. If full diagonalization is used, i.e., the option DAVIDSON is not used, then the oscillator strength sums are exact for the orbital basis set. In particular, this means that the dipole polarizability calculated as an oscillator strength sum is an analytic derivative value which should agree with the dipole polarizability found by the finite difference or other method. Note that if the Tamm-Dancoff approximation is used, the oscillator strength sums no longer are exact. The Tamm-Dancoff approximation [28, 32] actually can improve the quality of computed excitation energies when the molecular geometry is far from the equilibrium geometry.

C. DEMON2K@GRENOBLE

These keywords are described in documents available on

https://sites.google.com/site/markcasida/demon-grenoble

Keyword **EXCIT**ATION **TDA**

This keyword activates the TDDFT calculation of the excited states and specifies the options of the calculation. If the option TDA is present, then the Tamm-Dancoff approximation will be used. The default is not to use the TDA. Examples

• EXCITATION

The excitation energies and oscillator strengths are found by solving Casida's equation. Transition energies ω_k , oscillator strengths f_k defined by (14) and the expansion coefficients $\mathbf{c}^{(k)}$ (18) will be printed out for first few excited states. If full diagonalization is used, the oscillator strength sums are exact for the orbital basis set used. In particular, this means that the dipole polarizability calculated as an oscillator strength sum is an analytic derivative value which should agree with the dipole polarizability found by the finite difference (or other) method.

• EXCITATION TDA

The excitation energies and oscillator strengths are found by solving Casida's equation in the Tamm-Dancoff approximation (21). Transition energies ω_k , oscillator strengths f_k defined by (14) and the expansion coefficients $c^{(k)}$ (18) will be printed out for first few excited states. Note that, even if full diagonalization is used, the oscillator strength sums no longer exact for the orbital basis set used. In particular, this means that the dipole polarizability calculated as an

oscillator strength sum is not expected to agree with the dipole polarizability found by the finite difference (or other) method.

Keyword DAVIDSON EIG=nwant BAS=nmatr MAX=maxit TOL=tol

This keyword specifies that the Davidson algorithm will be used and controls the options of the calculations. It has three parameters, two of which take integer values (nwant and nmatr) and one of which takes a real value (tol).

- EIG=<Integer> number of the lowest excited states to be assumed in calculations. The default value is 10.
- BAS=<Integer> maximal size of the basis to be used in the iterative procedure, i.e. the size of the matrix to be diagonalized is $N_{matr} \times N_{matr}$. One should have in mind that $N \gg N_{matr} \ge N_{want}$. The default value is 20.
- MAX=<Integer> maximal number of iterations to be passed until the complete convergence of the iterative procedure is achieved. Usually the number of iterations required should increase with increasing the N_{want} and N_{matr} parameters. The default value is 100.
- TOL=<Real> the convergence accuracy criterium. The default value is 10^{-5} .

Example:

DAVIDSON EIG=10 BAS=30 MAXER=100 TOL=1.E - 6

This line requests that energies ω_k , oscillator strengths f_k and expansion coefficients $\mathbf{c}^{(k)}$ for $N_{want} = 10$ The basis size to be employed in the Davidson's scheme is equal either to $N_{matr} = 30$ or $N_{matr} = N_{matr}^{\uparrow} + N_{matr}^{\downarrow} = 60$, respectively. The iterative procedure will continue either until the complete convergence is achieved with an error of 10^{-6} or until 100 iterations have been made.

Undocumented keywords

Several keywords (or options to keywords) are undocumented. These are briefly described here. In general an undocumented keyword is undocumented for a reason (either it does not yet work or it has not been explicitly tested.)

The keyword EXCIT has an option TDDIA which allows the user to specify which diagonalization method is used for solving Casida's equation. Options are RS, DYSEVD, DSYEV, JACOB, and DAVIDSON. (This last option is evidently redundant.) Not all options have been tested.

The keyword DOUBLE requests the explicit double excitations using polarization propagator corrections according to Ref. [19]. This option is being worked on and is not yet available. The keyword NONCOL requests the calculation of excitation energies and oscillator strengths using noncollinear spin-flip TDDFT [21]. This option is being worked on and is not currently available. Keyword

Keyword **NONCOL**

This keyword activates the Spin-Flip calculation. No options are present. Note that this keyword can only be used together with the keyword **EXCIT**. For **EXCIT** the **TDA** option is automatically selected in the case of a Spin-Flip calculation. The options **SING**, **TRIP** and **BOTH** are not active.

The keyword **SYMMETRY ON** activates spatial-symmetry-based calculations for spin-unrestricted calculations. This keyword must occur in the input before the **GEOMETRY** keyword. The **CARTESIAN** keyword is mandatory because symmetry adapted linear combination (SALC) construction assumes 6d rather than 5d functions. Molecular orbital (MO) symmetry assignments for the tight-binding **TB** guess have not been implemented in DEMON2K, so that the **SYMMETRY ON** keyword must be accompanied by the **GUESS CORE** option. Thus calculations requesting orbital symmetry assignments must have the keyword, **SYMMETRY ON** along with the **ORBITAL CARTESIAN** and **GUESS CORE** options.

The restriction to **CARTESSIAN** and **GUESS CORE** may be considered minor bugs which we hope will be fixed in the future.

V. ACKNOWLEDGMENTS

We would like to thank Antony Fouqueau, Christine Jamorski Jödicke, Andrei Ipatov, Loïc Joubert Doriol, Pierre Girard, and all the DEMON developers.

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