



**Short Course on Density Functional Theory
and Applications
VIII. Time-dependent DFT**

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Time-dependent Schrödinger Equation and DFT

The time-dependent many-electron Schrödinger equation is

$$i \frac{\partial \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e}, t)}{\partial t} = \hat{\mathcal{H}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e}, t) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e}, t)$$
$$\hat{\mathcal{H}}(\mathbf{r}_1, \dots, \mathbf{r}_{N_e}, t) = -\frac{1}{2} \sum_{i=1}^{N_e} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i^{N_e} v_{ext}(\mathbf{r}_i, t)$$

There is no easy, straightforward analogue to the stationary state variation principle that leads to the TDSE. There is a stationary action principle, but in its basic form, it turns out to lead to a logical contradiction for TDDFT. The resolution of that requires sophisticated technique. Thus it is not easy to imagine proving time-dependent analogues to HK-I, -II by some version of Levy-Lieb constrained search. (Remark: there are time-dependent variation principles, but such formulations have not played a significant role in mainstream TDDFT.)

Rudiments of the Runge-Gross Theorem Proof

- Instead of a constrained search, the Runge-Gross theorem [Phys. Rev. Lett. 52, 997 (1984)] proves the bijective mapping $v_{ext}(\mathbf{r}, t) \leftrightarrow n(\mathbf{r}, t)$

- Compared to stationary state DFT, the proof of the Runge-Gross Theorem is dependent on rather detailed arguments. Here, therefore, is a sketch. As usual, one direction of the invertibility, from v to n , is obvious.

A. Assume two external potentials that differ by more than a purely time-dependent function $v_A(\mathbf{r}, t) - v_B(\mathbf{r}, t) = f(\mathbf{r}, t) \neq f(t)$

B. Assume that each external potential has a well-behaved Taylor series expansion in time

$$v_{ext}(\mathbf{r}, t) = \sum_{j=0}^{\infty} \frac{1}{j!} \left. \frac{\partial^j v(\mathbf{r}, t)}{\partial t^j} \right|_{t=t_0} (t-t_0)^j$$

C. Assume that the initial state is specified with given initial density (here chosen to be a ground state).

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e}, t_0) = \Psi_0(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e}), \quad n(\mathbf{r}, t_0) = n_0(\mathbf{r})$$

Rudiments of the Runge-Gross Theorem Proof (cont'd.)

- **Part (1) of the proof – Demonstrate that the current densities corresponding to the two potentials differ**

$$\hat{\mathbf{j}}(\mathbf{r}) = \frac{-i}{2} \sum_{j=1}^N [\nabla_j \delta(\mathbf{r} - \mathbf{r}_j) + \delta(\mathbf{r} - \mathbf{r}_j) \nabla_j]$$

$$\mathbf{j}_\psi(\mathbf{r}, t) = \langle \psi(t) | \hat{\mathbf{j}}(\mathbf{r}) | \psi(t) \rangle$$

$$\mathbf{j}_A(\mathbf{r}, t > t_0) \neq \mathbf{j}_B(\mathbf{r}, t > t_0)$$

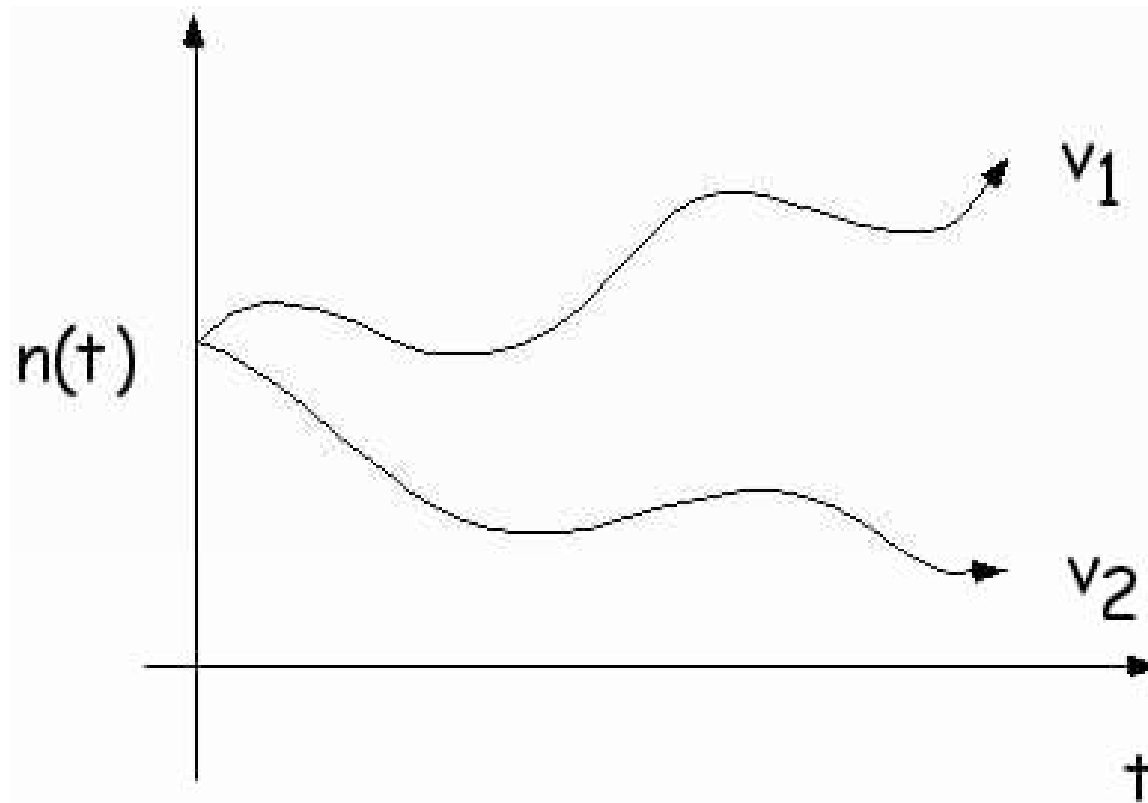
- **Part (2) of the proof – Use the equation of continuity to relate the time-dependent currents to the time-dependent densities.**

$$\frac{\partial n_\ell(\mathbf{r}, t)}{\partial t} = -\nabla \cdot \mathbf{j}_\ell(\mathbf{r}, t); \quad \ell = A, B$$

(Use the divergence theorem to show that a critical surface integral vanishes for all physically reasonable densities.) Since the current densities differ, one can prove that the charge densities must also.

- **Therefore the Runge-Gross result:** $v_{ext}(\mathbf{r}, t) = v_{ext}[n; \Psi_0](\mathbf{r}, t); \quad t \geq t_0$

Rudiments of the Runge-Gross Theorem – Pictorial Representation



- **Start at a known state, with a known density. Two time-dependent potentials that differ by more than a pure function of time generate two different densities for all $t > t_0$**

Credit: R van Leeuwen

Implications of the Runge-Gross Theorem

- **The external potential is a rather different object from that found in the stationary state case. It depends on both the history of the density and the initial state.**

$$v_{ext}(\mathbf{r}, t) = v_{ext}[n; \Psi_0](\mathbf{r}, t); \quad t \geq t_0$$

- **IF part of the knowledge of the history is that the initial state is known to be non-degenerate, then by appeal to stationary state DFT, one can say that**

$$v_{ext}(\mathbf{r}, t) = v_{ext}[n](\mathbf{r}, t); \quad t \geq t_0$$

- **By doing the Runge-Gross invertibility argument with explicit spin labels, one can get a spin-polarized TDDFT with**

$$v_{ext}(\mathbf{r}, t) = v_{ext}[n_\alpha, n_\beta; \Psi_0](\mathbf{r}, t); \quad t \geq t_0$$

- **The Runge-Gross argument does not depend upon the presence or absence of the electron-electron Coulomb interaction, \mathcal{V}_{ee} .**
- **Therefore a time-dependent KS scheme seems feasible.**

Credit: K. Burke



Time-dependent Kohn-Sham Equation

- Because there is no universal functional in the R-G proof analogous with HK-II, we cannot go through a time-dependent analogue of the KS rearrangement. Instead, we *assume* non-interacting v -representability for all times for the density and apply the R-G theorem to the non-interacting system. The result is TD-KS:

$$v_s(\mathbf{r}, t) \leftrightarrow n(\mathbf{r}, t)$$

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

$$i \frac{\partial \varphi_j}{\partial t} = [-\nabla^2 + v_s[n](\mathbf{r}, t)] \varphi_j$$

$$v_s[n](\mathbf{r}, t) = v_{ext}(\mathbf{r}, t) + \int d\mathbf{r}' \frac{n(\mathbf{r}', t)}{|\mathbf{r}' - \mathbf{r}|} + v_{xc}(\mathbf{r}, t)$$

- v_{xc} is defined to be the object needed to make these equations work. No independent information is provided about its properties or behavior, In particular, introducing the K-S system on the basis of the invertible mapping provides no information about functional derivatives. Specifically, one would *like* to know that v_{xcKS} is the functional derivative of a QM action. The obvious answer to that is wrong; see below.

Extended Runge-Gross Theorem

R. van Leeuwen [Phys. Rev. Lett. 82, 3863 (1999); Internat. J. Mod. Phys. B 15, 1969 (2001)] has given an extension of the R-G theorem which can be summarized as follows.

- Consider two systems, A, B , with differing two-body interactions and with differing external potentials.
- Require that at t_0 they have the same density and the same first derivative with respect to time of the density

$$n_A(\mathbf{r}, t_0) = n_B(\mathbf{r}, t_0); \quad \left. \frac{\partial n_A(\mathbf{r}, t)}{\partial t} \right|_{t_0} = \left. \frac{\partial n_B(\mathbf{r}, t)}{\partial t} \right|_{t_0}$$

- Then continuity arguments lead to a prescription for constructing all the time derivatives of the external potential of system B being identical with those of system A

$$\left. \frac{\partial^j v_{ext,A}(\mathbf{r}, t)}{\partial t^j} \right|_{t=t_0} = \left. \frac{\partial^j v_{ext,B}(\mathbf{r}, t)}{\partial t^j} \right|_{t=t_0}$$

- If system A is the physical system and B is the Kohn-Sham system, then this procedure, at least in principle, is a constructive approach to the KS potential.

TD-KS Potential as Functional Derivative of Something

- The obvious way to get to a functional analogous with the Levy-Lieb $F[n]$ in time-independent DFT would be via what is called a quantum-mechanical action:

$$A[\psi] = \int_{t_0}^t dt' \langle \psi | i \frac{\partial}{\partial t'} - \hat{\mathcal{H}}(t') | \psi \rangle$$

- Making this stationary with respect to variations in ψ leads, under suitable conditions, to the time-dependent Schrödinger equation.
- A straightforward generalization of the time-independent approach then would be to assume

$$A[n] = \int_{t_0}^t dt' \langle \psi[n] | i \frac{\partial}{\partial t'} - \hat{\mathcal{H}}(t') | \psi[n] \rangle$$

and attempt to prove that
$$\frac{\delta A[n]}{\delta n(\mathbf{r}, t)} = v_{ext}(\mathbf{r}, t)$$

Originally, it was argued that this could be done. *If so*, then we could set up a non-interacting system with the same density (KS system), use the corresponding action, etc. *Unfortunately*, no such functional exists for real physical time. There *is* an action in “Keldysh pseudo-time” that gets the job done, so $v_{xc}(\mathbf{r}, t)$ is the functional derivative of something. See van Leeuwen reference cited.

Approximate Time-dependent XC Functionals

Because of the complexity of the density-potential mapping (history dependence), construction of approximate functionals is much harder in TDDFT than in DFT. The most common approach is “adiabatic”:

$$E_{xc,approx} = \int d\mathbf{r} n(\mathbf{r}) u_{xc,approx} [n(\mathbf{r})] \Rightarrow v_{xc,approx}(\mathbf{r}) = \frac{\delta E_{xc,approx}}{\delta n(\mathbf{r})}$$

$$v_{xc,approx}(\mathbf{r}, t) \approx v_{xc,approx} [n(\mathbf{r}, t)] \quad \text{adiabatic approximation}$$

Of course, this approach completely loses the history dependence. The most common version is “adiabatic LDA”. There has been other work on approximate functionals but with nowhere near the breadth nor success as in the stationary state case.

Time-dependent XC Linear Response

At various points we have commented on the difficulty of getting one-electron energies in ground-state DFT. Since the Fourier transform of a time is an energy in QM, TDDFT provides an alternative route to address the problem.

First a sketch of linear response. Suppose a system which has its initial 1-rdm in a basis and its unperturbed time evolution given by

$$\gamma^0(1' | 1) = \sum_{ij} \mathcal{P}_{ij}^0 \Xi_j^*(1') \Xi_i(1)$$

$$\Psi_0(t) = \exp(-iE_0 t) \Psi_0$$

The linear response of the density matrix (in the basis) \mathcal{P} to an applied, time-dependent potential is

$$\delta \mathcal{P}_{ij}(t) = \sum_{k,l} \int_{-\infty}^{\infty} dt' \chi_{ij,kl}(t-t') \delta v_{app,kl}(t')$$

$$\delta v_{app}(t) = \sum_{ij} \delta v_{app,ij}(t) \Xi_j^*(1) \Xi_i(1)$$

Generalized
susceptibility

Reminder: time-frequency Fourier transforms and the convolution theorem:

$$f(\omega) = \int_{-\infty}^{\infty} dt e^{+i\omega t} f(t); \quad f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{-i\omega t} f(\omega)$$

$$s(t) = \int_{-\infty}^{\infty} dt' f(t') g(t-t') \Leftrightarrow s(\omega) = f(\omega) g(\omega)$$

Time-dependent XC Linear Response (cont'd.)

Therefore, the frequency dependent linear response of the density matrix (in the basis) \mathcal{P} to an applied, time-dependent potential is

$$\delta\mathcal{P}_{ij}(\omega) = \sum_{k,\ell} \chi_{ij,k\ell}(\omega) \delta v_{app,k\ell}(\omega)$$

Since this is for the density matrix, the result obviously also holds for the spin densities (sum over the basis: eliminates indices, restores spatial dependence)

$$\delta n_{\sigma}(\mathbf{r}, \omega) = \sum_{\sigma'} \int d\mathbf{r}' \chi_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}', \omega) \delta v_{app}(\mathbf{r}', \omega)$$

We require that the density response of the KS system be the same as the physical system. But the KS susceptibility is known, because it is for an independent particle system:

$$\chi_{S\sigma\sigma'}(\mathbf{r}, \mathbf{r}', \omega) = \delta_{\sigma\sigma'} \sum_{i,a} \left\{ \frac{\varphi_{i\sigma}^*(\mathbf{r}) \varphi_{a\sigma}(\mathbf{r}) \varphi_{a\sigma'}^*(\mathbf{r}') \varphi_{i\sigma'}(\mathbf{r}')}{\omega - (\varepsilon_{a\sigma} - \varepsilon_{i\sigma}) + i0^+} - \frac{\varphi_{i\sigma}(\mathbf{r}) \varphi_{a\sigma}^*(\mathbf{r}) \varphi_{a\sigma'}(\mathbf{r}') \varphi_{i\sigma'}^*(\mathbf{r}')}{\omega + (\varepsilon_{a\sigma} - \varepsilon_{i\sigma}) - i0^+} \right\}$$

The orbitals and eigenvalues are the Unperturbed KS ones. Orbitals “i” are occupied, “a” are empty in the KS ground state.

Credit: K. Burke



Time-dependent XC Linear Response (cont'd.)

The density response of the KS potential can be written as

$$n_{\sigma}(\mathbf{r}, t) = \sum_{j=1} n_{j\sigma} |\varphi_{j\sigma}(\mathbf{r}, t)|^2; \quad i \frac{\partial \varphi_{j\sigma}}{\partial t} = \left\{ -\nabla^2 + v_s[n_{\alpha}, n_{\beta}](\mathbf{r}, t) \right\} \varphi_{j\sigma}$$

$$v_s[n_{\alpha}, n_{\beta}](\mathbf{r}, t) = v_{Ne}(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}, t)}{|\mathbf{r}' - \mathbf{r}|} + v_{xcKS}[n_{\alpha}, n_{\beta}](\mathbf{r}, t) + v_{app}(\mathbf{r}, t) \\ := v_H(\mathbf{r}, t) + v_{xc}[n_{\alpha}, n_{\beta}](\mathbf{r}, t) + v_{app}(\mathbf{r}, t)$$

$$\delta(v_H(\mathbf{r}\sigma, t) + v_{xc}(\mathbf{r}\sigma, t)) = \sum_{\sigma'} \int d\mathbf{r}' dt' f_{\sigma\sigma'}^{Hxc}(\mathbf{r}, \mathbf{r}', t - t') \delta n_{\sigma'}(\mathbf{r}'t')$$

$$f_{\sigma\sigma'}^{Hxc}(\mathbf{r}, \mathbf{r}', t - t') = \frac{\delta v_H(\mathbf{r}\sigma, t)}{\delta n_{\sigma'}(\mathbf{r}'t')} + f_{\sigma\sigma'}^{xc}(\mathbf{r}, \mathbf{r}', t - t') = \frac{\delta(t - t')}{|\mathbf{r} - \mathbf{r}'|} + f_{\sigma\sigma'}^{xc}(\mathbf{r}, \mathbf{r}', t - t')$$

Putting it all together → self-consistent integral equation for the physical response

$$\chi_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}', \omega) = \chi_{S\sigma\sigma'}(\mathbf{r}, \mathbf{r}', \omega) + \sum_{\sigma_A \sigma_B} \int d\mathbf{r}'' d\mathbf{r}''' \chi_{S\sigma\sigma_A}(\mathbf{r}, \mathbf{r}'', \omega) \times \\ \left\{ \frac{1}{|\mathbf{r}'' - \mathbf{r}'''} + f_{\sigma_A \sigma_B}^{xc}(\mathbf{r}'', \mathbf{r}''', \omega) \right\} \chi_{\sigma_B \sigma'}(\mathbf{r}''', \mathbf{r}', \omega)$$

Credit: K. Burke

Time-dependent XC Linear Response (cont'd.)

Remarks:

1. The so-called “xc kernel” $f^{xc}(\mathbf{r},\mathbf{r}',\omega)$ is simpler than $v_{xc}[n(\mathbf{r},t)]$ because the kernel depends only on the ground-state density.
2. However, the kernel is non-local *both* spatially and temporally.
3. Setting the xc kernel to zero is equivalent to making the random phase approximation.
4. In general the xc kernel is complex; its real and imaginary parts are related by a Kramers-Kronig transformation.
5. Burke, Werschnik, and Gross [J. Chem. Phys. 123, 062206 (2005)] list four “deadly sins”, i.e. , serious problems for use of TDDFT
 - (a) Errors in the underlying ground-state DFT calculation: if the KS eigenvalues are in serious error, the TDDFT response functions will be do.
 - (b) Locality errors: use of one-point functionals forces locality on an inherently two-point object f_{xc}
 - (c) Forgetfulness errors: the adiabatic approximation inherently mistreats phenomena for which history (temporal trajectory) are important
 - (d) Wavefunction errors: even the exact v_{xc} does not deliver the exact wavefunction, only the KS wavefunction. The two are NOT equivalent.

TDDFT – Examples of two of the “Four Sins”

At Lect. IV-6, we discussed the error in the asymptotic form of the KS potential that arises from LSDA and GGA. It falls off exponentially, not as $1/r$. For example, here it is for the He atom

For certain transitions in certain systems, failure to remedy (or at least patch) this incorrect asymptotic behavior can lead to very bad TDDFT results or even total failure.

The adiabatic approximation for v_{xc} automatically removes the possibility of treating double excitations (because the history of the system is lost at every instant).

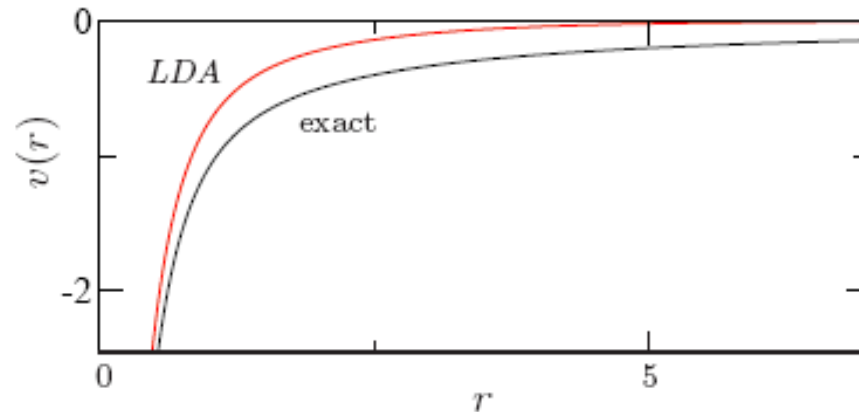


FIG. 3: Exact and LDA KS potentials for the He atom. While the exact potential falls off as $-1/r$, the LDA decays much too quickly. This is common for nearly all present functionals and has major consequences for TDDFT.

Credit: K. Burke

TDDFT Linear Response – Excitation Energies

Now go back to the expansion in a basis, using the unperturbed KS orbitals [Casida, *Recent Advances in Density Functional Methods, Part I*, D.P. Chong, ed. (World Scientific, Singapore, 1995), 155-192] to get an expression for the excitation energies of the physical system. The result is a set of matrix equations

$$\left\{ \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} - \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} \right\} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = - \begin{pmatrix} \delta v(\omega) \\ \delta v^*(\omega) \end{pmatrix}$$

The \mathbf{X} and \mathbf{Y} matrices are the density matrices in the basis. The \mathbf{A} and \mathbf{B} matrices are messy objects, the main component of which is

$$K_{ia\sigma, jb\sigma'}(\omega) = \int d\mathbf{r} d\mathbf{r}' \varphi_{i\sigma}^*(\mathbf{r}) \varphi_{a\sigma}(\mathbf{r}) f_{\sigma\sigma'}^{Hxc}(\mathbf{r}, \mathbf{r}', \omega) \varphi_{j\sigma'}^*(\mathbf{r}') \varphi_{b\sigma'}(\mathbf{r}')$$

After further manipulation, an eigenvalue equation for the frequencies ω emerges

$$\Omega \mathbf{a} = \omega^2 \mathbf{a}$$

$$\Omega = (\mathbf{A} - \mathbf{B})^{1/2} (\mathbf{A} + \mathbf{B})^{1/2} (\mathbf{A} - \mathbf{B})^{1/2}$$

TDDFT vs. KS – Exact One-electron Excitations

For atomic He it is possible to construct the exact KS potential and the exact TDKS potential, hence compare the one electron eigenvalues of the former with the predicted excitation energies of the latter. [arXiv:cond-mat/0703590]

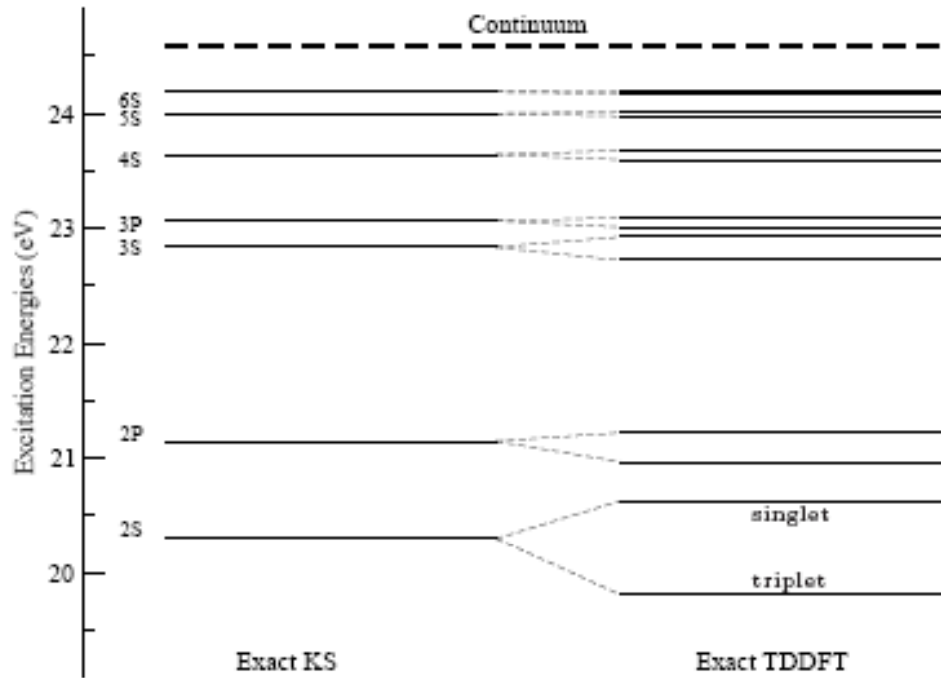


FIG. 4: Transitions for the Helium atom using in ground-state DFT on the left, and TDDFT on the right. In both cases, the exact functionals have been used. The results for employing the exact XC kernel in TDDFT linear response are known from calculations using Ref. [192]. In each pair of lines on the right, the triplet is the lower.

TDDFT Linear Response – Excitation Energies (cont'd)

Here are some adiabatic LDA results from Grabo et al. [J. Molec. Struct. (Theochem) **501**, 353 (2000)]. SPA= “single pole approx.” (a truncation of the matrix equations) SMA=“small matrix approx.” (a truncation involving a process $i \rightarrow j$ and its converse).

Table 2

Excitation energies for N_2 from an xcLDA-calculation at $R = 2.0744$ a.u. The LDA was employed for V_{xc} and the ALDA for the xc kernels. $\Delta\omega_{KS}$ denotes the KS orbital energy difference. All numbers in mHartrees

State		$\Delta\omega_{KS}$	SPA	SMA	Full ^a	Full ^b	Exp ^c
a $^1\Pi_g$	$3\sigma_g \rightarrow 1\pi_g$	301.4	344.3	341.6	339.4	334.4	342.1
B $^3\Pi_g$			281.0	280.2	280.1	279.3	295.5
a' $^1\Sigma_u^-$	$1\pi_u \rightarrow 1\pi_g$	355.8	355.8	355.8	355.8	355.0	364.6
B' $^3\Sigma_u^-$			355.8	355.8	355.8	355.0	355.4
A $^3\Sigma_u^+$			301.6	296.7	296.7	289.6	284.5
w $^1\Delta_u$			378.3	377.6	377.6	375.6	377.4
W $^3\Delta_u$			328.7	327.6	327.6	324.5	326.3
a'' $^1\Sigma_g^+$	$3\sigma_g \rightarrow 4\sigma_g$	381.1	385.3	385.3	385.3	–	448.3
E $^3\Sigma_g^+$			379.9	379.8	379.8	–	441.0
o $^1\Pi_u$	$2\sigma_u \rightarrow 1\pi_g$	412.5	521.3	509.8	509.8	–	500.9
C $^3\Pi_u$			384.9	383.9	383.7	380.7	411.2
c $^1\Pi_u$	$1\pi_u \rightarrow 4\sigma_g$	435.5	435.4	435.3	435.3	–	474.1
$^3\Pi_u$			434.8	434.8	434.9	–	470.3

^a Neglecting continuum states.

^b Basis-set calculation including continuum states from Ref. [33].

^c From Ref. [43].

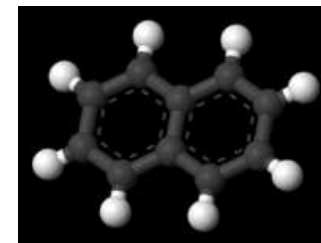
TDDFT Linear Response – Excitation Energies and Oscillator Strengths

TABLE IV: Performance of various density functionals for the first six singlet excitation energies (in eV) of naphthalene. An aug-TZVP basis set and the PBE/TZVP/RI ground-state structure was used. The “best” estimates of the true excitations were from experiment and calculations, as described in text.

Method	1^1B_{3u}	1^1B_{2u}	2^1A_g	1^1B_{1g}	2^1B_{3u}	1^1A_u
Pure density functionals						
LSDA	4.191	4.026	5.751	4.940	5.623	5.332
BP86	4.193	4.027	5.770	4.974	5.627	5.337
PBE	4.193	4.031	5.753	4.957	5.622	5.141
Hybrids						
B3LYP	4.393	4.282	6.062	5.422	5.794	5.311
PBE0	4.474	4.379	6.205	5.611	5.889	5.603
“best”.	4.0	4.5	5.5	5.5	5.5	5.7

TABLE V: Performance of various wavefunction methods for the excitations of Table I. The aug-TZVP basis set and the PBE/TZVP/RI ground-state structure was used for all except the CASPT2 results, which were taken from Ref. [197]. Experimental results are also from Ref. [197].

Method	1^1B_{3u}	1^1B_{2u}	2^1A_g	1^1B_{1g}	2^1B_{3u}	1^1A_u
CIS	5.139	4.984	7.038	6.251	6.770	5.862
CC2	4.376	4.758	6.068	5.838	6.018	5.736
CASPT2	4.03	4.56	5.39	5.53	5.54	5.54
expt.	3.97, 4.0	4.45, 4.7	5.50, 5.52	5.28, 5.22	5.63, 5.55	5.89
“best”.	4.0	4.5	5.5	5.5	5.5	5.7



Naphthalene: $C_{10}H_8$

TABLE VI: Performance of various density functionals and correlated wavefunction methods for the oscillator strengths of the first three dipole-allowed transitions of naphthalene. A aug-TZVP basis set and the PBE/TZVP/RI ground-state structure was used for all except the CASPT2 results, which were taken from Ref. [197].

Method	1^1B_{3u}	1^1B_{2u}	2^1B_{3u}
LSDA	0.0000	0.0405	1.1517
BP86	0.0000	0.0411	1.1552
PBE	0.0000	0.0407	1.1402
B3LYP	0.0000	0.0539	1.2413
PBE0	0.0000	0.0574	1.2719
LHF/LSDA	0.0000	0.0406	1.2089
LHF/PBE	0.0000	0.0403	1.2008
CIS	0.0002	0.0743	1.8908
CC2	0.0000	0.0773	1.4262
CASPT2	0.0004	0.0496	1.3365
expt.	0.002	0.102, 0.109	1.2, 1.3

CC2: modified CCSD

CASPT2: complete active space 2nd order PT

Some of these levels are hard to get by any method

[arXiv:cond-mat/0703590]

Some Commentary

- **The fact that the Runge-Gross proof depends on the external potential having a Taylor series in time with non-vanishing convergence radius bothers me. It seems inappropriately fussy compared to the elegance of the ground state HK theorems. It also seems to be a requirement that is violated for the case of moving nuclei.**
- **The vanishing of the surface integral that is required to complete step 2 of the Runge-Gross proof has attracted a significant amount of discussion. My opinion is that the issue has not been resolved satisfactorily, but few people seem to worry about it.**
- **The comparative lack of progress on TDDFT functionals and XC kernels is a sign of how hard it is to develop these.**
- **Because the TD-KS problem is time propagation, not SCF, and because there are response functions to evaluate, there are different demands on basis sets.**
- **It is possible to write TD-KS in the form of propagation of the time-dependent TDKS 1-rdm in a von Neumann equation. This is claimed to have some technical advantages.**