DYNAMICAL DETUNING OF RABI OSCILLATIONS IN ADIABATIC TIME-DEPENDENT DENSITY FUNCTIONAL THEORY

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Abstract

We show that due to the non-linearity of the Kohn-Sham Schrödinger equation, Rabi oscillations in adiabatic time-dependent density functional theory are always detuned from the linear response resonance ω_0.
We have proven our hypothesis by studying a one-dimensional two-electron singlet system that can be solved exactly. The system is mapped into a non-interacting Kohn-Sham one and an analytic expression for the dynamical detuning is found within the exact exchange approximation.

One-dimensional model system

The Hamiltonian for an interacting non-relativistic N-electron system coupled to a laser field of the form $\mathcal{E}(t) = \mathcal{E}_0 \sin(\omega t)$ in dipole approximation is given by

$$\hat{H} = \hat{T} + \hat{V}_{ext} + \hat{V}_{ee} + \sum_{j=1}^{N} \vec{r}_j \vec{\mathcal{E}}(t) \quad (1)$$

with $V_{ee} = \frac{1}{\sqrt{(\vec{r}-\vec{r}')^2+1}}$. Atomic units ($m_e = e = \hbar = 1$) are used.

Rabi oscillations and effective two-level system

- Rabi's solution of a two-level system interacting with a single frequency field predicts oscillations between the ground state ψ_g and an excited state ψ_e when the frequency ω of the applied field is close to the energy Δ of the transition.
- The frequency Ω of the Rabi oscillations depends on the amplitude $\mathcal{E}_0$ of the external field, on the transition matrix element $d_{eg} = <\psi_e|\sum_j \hat{r}_j|\psi_g>$ and on the detunning $\delta = \omega - \Delta$ as $\Omega = \sqrt{\delta^2 + (d_{eg}\mathcal{E}_0)^2}$. For the resonant case the Rabi frequency is just $\Omega_0 = d_{eg}\mathcal{E}_0$. (see for example [1]).
- The conditions in order to have an effective two-level system are the following,

$$\delta << \Delta, \quad \Omega_0 << \omega, \quad (2)$$

If these conditions are fullfilled the system can be considered an effective two-level system and the wavefunction can be written as a linear combination of ground and excited states as

$$|\psi(t)> = a_g(t)|\psi_g> + a_e(t)|\psi_e> \quad (3)$$

Rabi oscillations can be observed in the time-dependent populations of the ground and excited states,

$$|a_g(t)|^2 = n_g(t), \quad |a_e(t)|^2 = n_e(t) \quad (4)$$

and for a symmetric hamiltonian like the one in Eq. (1) also in the time-dependent dipole moment,

$$d(t) = \langle\psi(t)|\sum_j \hat{r_j}|\psi(t)\rangle = 2 d_{eg} Re(a_g^* a_e) \quad (5)$$

Normalization of the wavefunctions implies $n_g(t) + n_e(t) = 1$.

Rabi oscillations in the many-body interacting system

We project the hamiltonian Eq. (1) onto the 2×2 level space of Eq. (3) and let the system evolve according to the time-dependent Schrödinger Equation,

$$i\partial_t \begin{bmatrix} a_g \\ a_e \end{bmatrix} = \begin{bmatrix} \langle\psi_g|\hat{H}_0|\psi_g\rangle & \langle\psi_g|\hat{r}\mathcal{E}(t)|\psi_e\rangle \\ \langle\psi_e|\hat{r}\mathcal{E}(t)|\psi_g\rangle & \langle\psi_e|\hat{H}_0|\psi_e\rangle \end{bmatrix} \begin{bmatrix} a_g \\ a_e \end{bmatrix}$$

Assuming conditions Eq. (2) are fullfilled we profit from the timescale separation between the fast oscillatting external frequency ω and the slowly variying Rabi frequency Ω to use Rotating Wave Approximation (RWA). Solving the differential system brings us to an expression for the time-dependent dipole moment and leads to the following differential equation for the population $n_e(t)$ of the excited state,

$$\partial_t^2 n_e(t) = -\left(\delta^2 + \Omega_0^2\right) n_e(t) + \frac{1}{2}\Omega_0^2 \quad (6)$$

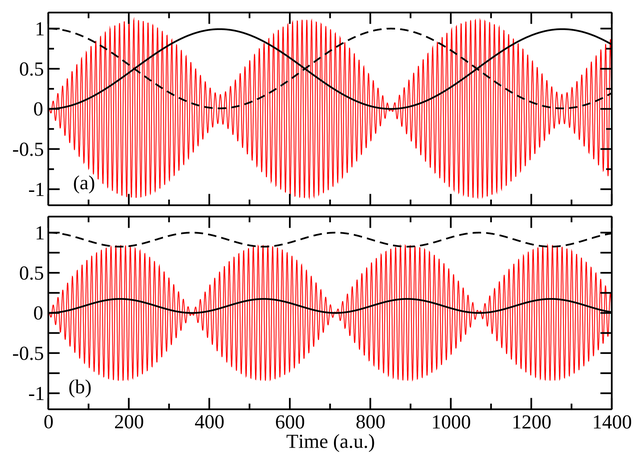

Fig. 1: *Dipole moment (red) and populations n_e (solid black line) and n_g (dashed black line) using $\mathcal{E}_0 = 0.0125\omega$ for detuning $\delta = 0.08\Omega_0$ (0.0006 Ha) (a) and $\delta = 2.2\Omega_0$ (0.016 Ha) (b).*

Rabi oscillations in the KS system

The time-dependent Kohn Sham (KS) hamiltonian has an additional term due to exchange-correlation and Hartree potentials $V_{hxc}[\rho(r,t)]$ being functionals of the time-dependent density.

$$\hat{H}_s = \hat{H}_s^0 + \hat{V}_{hxc}^{dyn}(t) + \hat{\mathbf{r}}\mathcal{E}(t) \quad (7)$$

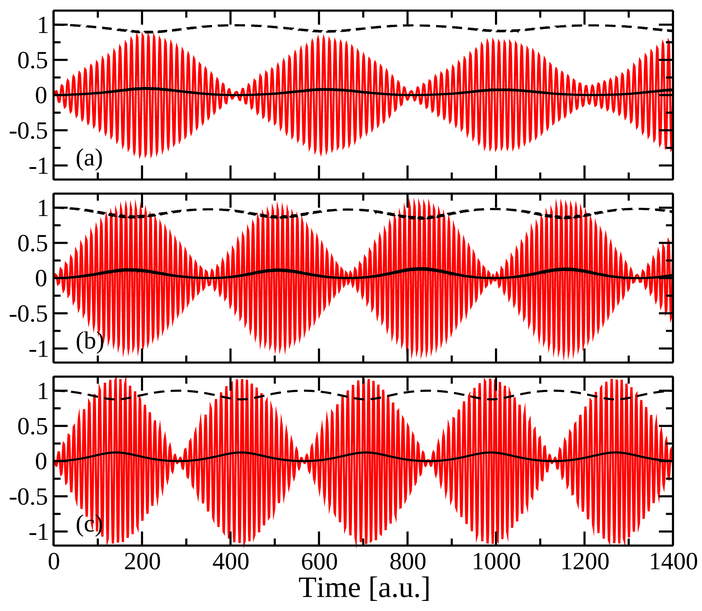

Fig. 2: *Dipole moment (red) and populations n_e^s (solid black line) and n_g^s (dashed black line) for LDA (a) and EXX (b) computed from numerical time propagation in* `octopus` *([2, 3]). The results from the theoretical model Eq. (10) are given in (c).*

Dynamical detuning within adiabatic EXX

We use here the exact exchange (EXX) functional to study a two-electron singlet system, for this case EXX is adiabatic and equal to Hartree-Fock,

$$V_{hxc}^{EXX}(x,t) = \frac{1}{2}\int d^3x \hat{V}_{ee}(|x-x'|)(\rho_0(x') + \delta\rho(x',t)) \quad (8)$$

The KS two-level expansion,

$$|\phi(t)> = a_g^s(t)|\phi_g> + a_e^s(t)|\phi_e> \quad (9)$$

leads to the following differential system after projection of hamiltonian Eq. (7),

$$i\partial_t \begin{bmatrix} a_g^s \\ a_e^s \end{bmatrix} = \begin{bmatrix} \langle\phi_g|\hat{H}_s^0 + \hat{V}_{hxc}^{dyn}(t)|\phi_g\rangle & \langle\phi_g|\hat{\mathbf{r}}\mathcal{E}(t) + \hat{V}_{hxc}^{dyn}(t)|\phi_e\rangle \\ \langle\phi_e|\hat{\mathbf{r}}\mathcal{E}(t) + \hat{V}_{hxc}^{dyn}(t)|\phi_g\rangle & \langle\phi_e|\hat{H}_s^0 + \hat{V}_{hxc}^{dyn}(t)|\phi_e\rangle \end{bmatrix} \begin{bmatrix} a_g^s \\ a_e^s \end{bmatrix}$$

Time evolution only affects one unique orbital and follows from the KS equation $i\partial_t\phi(\mathbf{r},t) = \hat{H}_s\phi(\mathbf{r},t)$.
Assuming conditions Eq. (2) are fullfilled and defining the resonance as the frequency of the linear response ω_0^{EXX} we again use RWA as in the linear case and end up with the following expression for the non-linear KS problem,

$$\partial_t^2 n_e^s(t) = -\left(\frac{\gamma^2}{2} n_e^s(t)^2 + \Omega_s^2\right) n_e^s(t) + \frac{1}{2}\Omega_s^2 \quad (10)$$

with $\gamma = (\lambda_e - \lambda_g) - 2g$ and $\Omega_s = d_{eg}^s \mathcal{E}_0$.

- $\lambda_{g,e} = \iint dx\, dx' \left(|\phi_e(x')|^2 - |\phi_g(x')|^2\right) \hat{V}_{ee}(|x-x'|)|\phi_{g,e}(x)|^2$.
- $g = \iint dx dx' \phi_e(x')\phi_g(x')\hat{V}_{ee}(|x-x'|)\phi_g(x)\phi_e(x)$.

Unlike Eq.(6) which corresponds to an harmonic oscillator, Eq.(10) corresponds to an anharmonic quartic oscillator, analytic solutions can be found in ([5]) or it can be solved numerically.

Conclusions

- From the results of the numerical time-propagation and from comparison of Eq.(6) and Eq.(10) we can conclude that there exist Rabi oscillations in adiabatic time-dependent density functional theory contrary to what is stated in [4] for the same system, and that they are always detuned.
- For any adiabatic functional the potential will change due to the changing density and the system is driven out of resonance. This effect is not limited to TDDFT but is generic for all mean-field theories, e.g. HF or all hybrids, when the effective potential depends instantaneously on the state of the system.
- Only the inclusion of an appropriate memory dependence can correct the fictitious time-dependence of the resonant frequency.
- Adiabatic functionals will fail similarly in the description of all processes involving a change in the population of states.

References

[1] David J. Tannor, "Introduction to Quantum Mechanics a time-dependent perspective", University Science books, (2007) , pages 479 – 482

[2] A. Castro *et al.*, Phys. Stat. Sol. (b) **243**, 2465 (2006).

[3] M. A. L. Marques, A. Castro, G. F. Bertsch, and A. Rubio, Comp. Phys. Comm. **151**, 60 (2003).

[4] M. Ruggenthaler and D. Bauer, Phys. Rev. Lett. **102**, 233001 (2009).

[5] A. Martin Sanchez, J. Daz Bejarano and D. Caceres Marzal, Journal of Sound and Vibration (1993) **161** (1) , 19-31

[6] J.I. Fuks, N. Helbig, I.V. Tokatly, A. Rubio, "Non-linear phenomena in time-dependent density-functional theory: What Rabi physics can teach us ", arXiv:1101.2880

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