Memory in Time-Dependent Density Functional Theory

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May 21, 2020

References

- Maitra, N. T., Burke, K., & Woodward, C. (2002). Memory in Time-Dependent Density Functional Theory. Phys. Rev. Lett. 89, 023002.
- CECAM Memory in TDDFT: https://www.youtube.com/watch?v=ZdNjTHBEEG8

What is memory?

- Motivation is to develop approximated time-dependent exchange-correlation potentials $v_{\mathrm{xc}}(\mathbf{r}, t)$
- The adiabatic approximation neglects all memory
- There are two forms of memory dependence which are the initial state dependence and the history dependence

Working System

Suppose a system with wavefunction $\Psi(0)$ at time $t = 0$ and evolves according to

$$\hat{H}(t)\Psi(t) = i\frac{\partial\Psi(t)}{\partial t} \quad (1)$$

$$\hat{H} = \hat{T} + w(|\mathbf{r} - \mathbf{r}'|) + v_{\text{ext}}(\mathbf{r}, t), \quad (2)$$

where $\hat{H}$ consist of the kinetic-energy operator $\hat{T}$, the particle-particle interaction w, and the time-dependent (TD) one-body external potential $v_{\text{ext}}(\mathbf{r}t)$.

$$n_0(\mathbf{rt}) = N\sum_{\sigma}\int dx_2 \cdots dx_N |\Psi(x, x_2, \cdots, x_N, t)|^2 \quad (3)$$

is the single-particle density with variables $x_i = (\mathbf{r}_i, \sigma_i)$.

Initial State Dependence

- Use Runge-Gross Theorem there is a one-to-one correspondence between the TD density $n(\mathbf{r}, t)$ and the external density $v_{\text{ext}}[n; \Psi_0](\mathbf{r}, t)$
- Similarly, the TD Kohn-Sham (KS) with the same density $n(\mathbf{r}, t)$ and corresponding KS potential $v_s[n; \Phi_0](\mathbf{r}, t)$

$$v_s[n; \Phi_0](\mathbf{r}, t) = v_{\text{ext}}[n; \Psi_0](\mathbf{r}, t) + v_{\text{H}}[n](\mathbf{r}, t) + v_{\text{xc}}[n; \Psi_0, \Phi_0](\mathbf{r}, t) \tag{4}$$

Initial State Dependence

- Since in most cases Ψ_0 is given by the problem at hand, a KS determinant Φ_0 can be chosen in such a way that

$$n_{\Phi_0}(\mathbf{r},t) = n_{\Psi_0}(\mathbf{r},t) \tag{5}$$

$$\frac{\partial n_{\Phi_0}(\mathbf{r},t)}{\partial t} = \frac{\partial n_{\Psi_0}(\mathbf{r},t)}{\partial t} \tag{6}$$

- Eqn (6) comes from the continuity equation $\partial n/\partial t = -\nabla j$
- Different choices of Φ_0 lead to different $v_{xc}(\mathbf{r},t)$

History Dependence

- $v_{xc}(\mathbf{r}, t)$ depends not only $n(\mathbf{r}, t)$ but also, the entire history
- Suppose starting the system at some intermediate time t', $0 < t' < t$, as the intial time and intial wavefunction $\Psi(t') = U(t')\Psi(0)$
- For $t \geq t'$,

$$v_{\text{ext}}[n_{t'}, \Psi(t')](\mathbf{r}, t) = v_{\text{ext}}[n_0, \Psi(0)](\mathbf{r}, t) \tag{7}$$

$$n_{t'}(\mathbf{r}, t) = n(\mathbf{r}, t) \tag{8}$$

$$v_s[n_{t'}, \Phi(t')](\mathbf{r}, t) = v_s[n_0, \Phi(0)](\mathbf{r}, t) \tag{9}$$

$$v_{\text{xc}}[n_{t'}, \Psi(t'), \Phi(t')](\mathbf{r}, t) = v_{\text{xc}}[n_0, \Psi(0), \Phi(0)](\mathbf{r}, t) \tag{10}$$

Thank You for Your Attention