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Excitation Energies from Ensemble DFT

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Abstract. We study the evaluation of the Gross-Oliveira-Kohn expression for excitation energies

$$E_1 - E_0 = \varepsilon_1 - \varepsilon_0 + \left.\frac{\partial E_{xc,w}[\rho]}{\partial w}\right|_{\rho=\rho_0}.$$

This expression gives the difference between an excitation energy $E_1 - E_0$ and the corresponding Kohn–Sham orbital energy difference $\varepsilon_1 - \varepsilon_0$ as a partial derivative of the exchange-correlation energy of an ensemble of states $E_{xc,w}[\rho]$. Through Lieb maximisation, on input full-CI density functions, the exchange-correlation energy is evaluated accurately and the partial derivative is evaluated numerically using finite difference. The equality is studied numerically for different geometries of the H_2 molecule and different ensemble weights. We explore the adiabatic connection for the ensemble exchange-correlation energy. The latter may prove useful when modelling the unknown weight dependence of the exchange-correlation energy.

INTRODUCTION

Today Time-dependent Density-Functional Theory (TDDFT) [1] is the method of choice to study excitation energies. Current computer programs allow non-experts to use the method and gain valuable insight into the spectra of relatively large molecules. However, the adiabatic approximation of standard TDDFT renders it unsuitable for studying an important class of systems exhibiting near-degeneracies such as those in conical intersections in photochemistry for instance. Therefore scientists today resort to costly wave-function approaches. The work here is towards the development of an alternative, Time-Independent DFT approach that can handle near-degeneracies.

Based on the extension of the familiar DFT to ensembles, Gross, Oliveira and Kohn (GOK),[2, 3, 4] showed that with a Hohenberg–Kohn theorem for ensembles and an extension of the usual Kohn-Sham approach, excitation energies can be evaluated as

$$E_1 - E_0 = (\varepsilon_1 - \varepsilon_0) + \left.\frac{\partial E_{xc,w}[\rho]}{\partial w}\right|_{\rho=\rho^w}, \tag{1}$$

where ε_1 and ε_0 are Kohn-Sham orbital energies and $E_{xc,w}[\rho]$ is the exchange-correlation energy of the ensemble with weight w. Note that the orbital energies in the equation are readily available from a regular Kohn–Sham DFT calculation and that, with an approximate density functional to model the weight dependence of $E_{xc,w}[\rho]$, excitation energies can be obtained straightforwardly. Although the original GOK derivation dates back to 1988, it has not yet lead to a practical method.

The aim of the present paper is to evaluate the terms in Eq. 1 exactly (full-CI), to gain insight into the behaviour of the exact exchange-correlation contribution. By formulating the theory in the context of Lieb's definition of the density functional [5] and carrying through the Lieb maximisation by generalising the established approaches for the ground state [6, 7], the newly developed computational tools allow a study of the adiabatic connection for ensembles [8], which could be used to construct new approximate functionals in analogy with the ground state situation.

THEORY

On the Lieb Ensemble Density Functional

Consider the density matrix of a statistical ensemble formed by a weighted combination of the M lowest states of the Hamiltonian in the Born–Oppenheimer approximation

$$\hat{\gamma}_{\lambda,w} = \sum_{i=1}^{M} w_i |\Psi_{\lambda,i}\rangle \langle \Psi_{\lambda,i}|, \tag{2}$$

where $\{w_i\}$ are decreasing coefficients such that $w_{i+1} \leq w_i$ and $\sum_i w_i = 1$, referred to as the ensemble weights, $|\Psi_{\lambda,0}\rangle$ is the ground and $|\Psi_{\lambda,i\geq1}\rangle$ are excited states of the Hamiltonian

$$\hat{H}_\lambda[V] = \hat{T} + \lambda\hat{W} + \hat{V}, \tag{3}$$

with interaction strength $0 \leq \lambda \leq 1$, a kinetic term

$$\hat{T} = -\frac{1}{2}\sum \nabla_i^2, \tag{4}$$

the scaled electron repulsion term

$$\lambda\hat{W} = \lambda\sum\frac{1}{r_{12}}, \tag{5}$$

and the external potential due to the nuclei

$$\hat{V} = \sum v(\mathbf{r}_i). \tag{6}$$

The mapping between ensemble densities and potentials can be studied in the context of Lieb's formulation of DFT [9] i.e. a pair of convex conjugate functionals relate the energy expectation value for a given potential $V(\mathbf{r})$ with the density functional

$$F_{\lambda,w}[\rho] = \sup_{V \in \mathscr{V}_N} E_{\lambda,w}[V] - \int \rho_{\lambda,w}(\mathbf{r})V(\mathbf{r})d\mathbf{r}, \tag{7}$$

and

$$\bar{E}_{\lambda,w}[V] = \inf_{\rho \in \mathscr{B}_N} F_{\lambda,w}[\rho] + \int \rho(\mathbf{r})V(\mathbf{r})d\mathbf{r} \tag{8}$$

where $\bar{E}_{\lambda,w}[V]$ is the convex hull of

$$E_{\lambda,w}[V] = \inf_{\gamma_w} \text{tr}\,\hat{\gamma}_w \hat{H}_\lambda[V] \tag{9}$$

To show that the ensemble energy in Eq. 9 is concave in V, we decompose it as a weighted combination of terms $S_i = \sum_{j=1}^{i} E_j[V]$

$$E_{\lambda,w}[V] = \sum_{i=1}^{M} w_i E_i[V] = \sum_{i=1}^{M} k_i S_i = \sum_{i=1}^{M} k_i \sum_{j=1}^{i} E_j[V] \tag{10}$$

Using the condition of decreasing weights w_i, k_i can easily be found. The concavity of the ensemble energy Eq. 9 now follows from the concavity of S_i [9] and the fact that a weighted combination of concave functions, with positive weights, is concave. The concavity of Eq. 9 is sufficient to define the conjugate pair of functionals 7 and 8 and study density functionals for these ensembles.

Lieb Maximisation in Practice

The Lieb maximisation approach for the ground states has been generalised to evaluate Eq. 7, opening the door to the investigation of DFT for ensembles and the right hand side of Eq. 1. Through an interface with the LUCITA CI code [10], the in house Lieb optimiser [6, 7] has been extended to evaluate Eq. 7 for input full-CI density functions.

In DFT for pure-state ground states significant insight into $E_{xc}[\rho]$ has been gained through a coupling constant integration or adiabatic connection. Here we extend the approach to establish an adiabatic connection to gain insight into the partial derivative term on the right hand side of Eq. 1.

The universal functional $F_{\lambda=1,w}[\rho]$ can be connected adiabatically to the non-interacting $F_{\lambda=0,w}[\rho]$

$$F_{\lambda=1,w}[\rho] = F_{\lambda=0,w}[\rho] + \int_{\lambda=0}^{\lambda=1} \frac{\partial F_{\lambda,w}[\rho]}{\partial \lambda} d\lambda = T_{s,w}[\rho] + \int_{\lambda=0}^{\lambda=1} d\lambda \, \mathrm{tr} \hat{\gamma}_{\lambda,w} \hat{W} \tag{11}$$

where $\hat{\gamma}_{\lambda,w}$ minimises

$$\inf_{\hat{\gamma}_{\lambda,w} \to \rho} \hat{\gamma}_{\lambda,w} \hat{H}_\lambda. \tag{12}$$

The familiar adiabatic connection for the ground state is thus generalised for ensembles and gives

$$E_{xc,w}[\rho] = \int_{\lambda=0}^{\lambda=1} d\lambda \, \mathrm{tr} \hat{\gamma}_{\lambda,w} \hat{W} - J[\rho] \tag{13}$$

Evaluating the partial derivative leads to

$$\left. \frac{\partial E_{xc,w}[\rho]}{\partial w} \right|_{\rho=\rho_w} = \left. \frac{\partial}{\partial w} \left(F_{\lambda=1,w}[\rho] - F_{\lambda=0,w}[\rho] \right) \right|_{\rho=\rho_w} - J[\rho_w] \tag{14}$$

or via the adiabatic connection

$$\left. \frac{\partial E_{xc,\lambda=1,w}[\rho]}{\partial w} \right|_{\rho=\rho_w} = \int_0^1 d\lambda \frac{\partial}{\partial w} \left(\mathrm{tr} \hat{\gamma}^{w\lambda} \hat{W} - J[\rho] \right)_{\rho=\rho_w} \tag{15}$$

Note that assumptions have to made concerning the existence of the adiabatic connection. We will study both expressions by using a finite difference approximation for the derivatives in both expressions above.

RESULTS AND DISCUSSION

In this section we study the first excitation energy of the H_2 molecule. The local nature of the first excited state allows optimiser to find the maximizing potentials to evaluate the Lieb functional. The presented results are based on the evaluation of the Lieb functional for full-CI input densities obtained with aug-cc-PVTZ basis set.

For a localised excitation in a compact molecule, it has been argued that the resemblance of the exchange-correlation hole and the depletion hole yield orbital energy differences that are close to the corresponding excitation energies [11]. From the lowest two full-CI (aug-cc-PVTZ) root energies for the H_2 molecule we found an excitation energy of 10.6 eV (0.389 a.u.) and a corresponding Kohn–Sham energy difference of 11.9 eV (0.437 a.u.). We note that the orbital energy difference from our method is closer to the triplet excitation than the singlet excitation energy, contrary to the value reported in Ref. 11.

In the left panel of Figure 1 we plot the excitation energy and the orbital energy differences as a function of the ensemble weight. The excitation energy is independent of the weight, but the orbital energy difference increases with the weight. The weight dependence of the latter follows from the weight dependence of the effective potential in the Kohn–Sham Hamiltonian. In the right hand panel of Figure 1 we plot the difference of the excitation energy and the orbital energy difference for three different geometries. From the latter we observe that by stretching the bond, for the pure state ($w = 0$), the difference initially becomes more negative, but then goes to zero as the two hydrogen atoms are separated and the two lowest eigenvalues become degenerate. For the *equiensemble* ($w = 0.5$) however, the difference between the excitation energy and the orbital energy difference monotonically decreases with increasing bond length, as expected. It is interesting to note that, unlike in the case of the He atoms [12] the difference is never equal to the excitation energy. The right hand panel of Figure 1 also shows the values of the partial derivative of the exchange-correlation energy with respect to the weight as evaluated with Eq. 14 and a finite difference approximation. Although there is a minor discrepancy (0.0211 eV) for the pure-state at equilibrium bond length, overall the GOK expression is confirmed accurately.
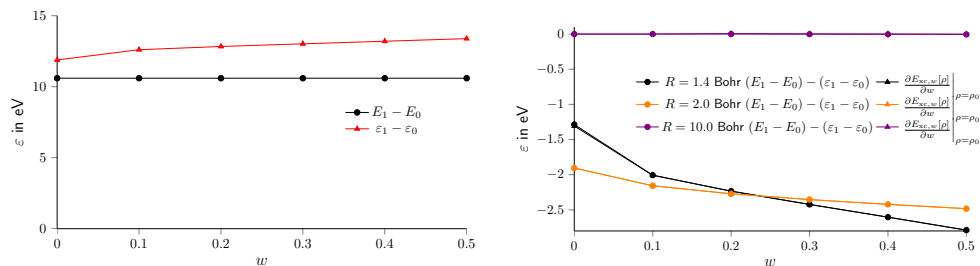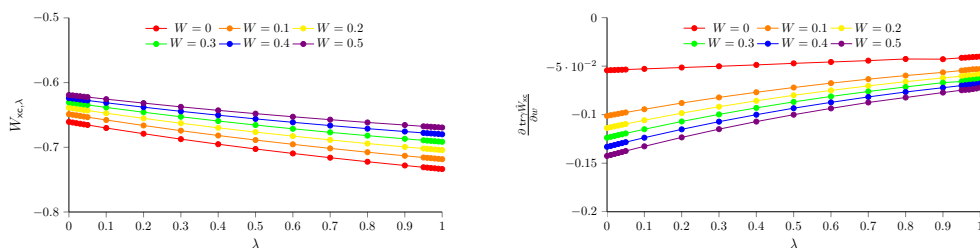
FIGURE 1.

FIGURE 2.

The left hand panel of Figure 2 shows a plot of the adiabatic connection, the integrand in Eq. 13 for the H_2 molecule at equilibrium bond length ($R = 1.4$ Bohr). The pure-state curve ($w = 0$) is the familiar ground state result. As the ensemble contains more of the excited-state component, the curve moves up, indicating that the ensemble exchange energy increases with the ensemble weight. The plot on the right hand side of Figure 2 contains the integrand of Eq. 15. This quantity that integrates to the partial derivative on the right hand side of the GOK expression in Eq.1. Modelling the curves in figure 2 would yield an approximate ensemble exchange-correlation functional with the correct weight dependence, suitable for evaluating excitation energies with Eq.1.

ACKNOWLEDGMENTS

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