

Optimization of constrained density functional theory

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Abstract

Constrained density functional theory (cDFT) is a versatile electronic structure method that enables ground-state calculations to be performed subject to physical constraints. It thereby broadens their applicability and utility. Automated Lagrange multiplier optimisation is necessary for multiple constraints to be applied efficiently in cDFT, for it to be used in tandem with geometry optimization, or with molecular dynamics. In order to facilitate this, we comprehensively develop the connection between cDFT energy derivatives and response functions, providing a rigorous assessment of the uniqueness and character of cDFT stationary points while accounting for electronic interactions and screening. In particular, we provide a new, non-perturbative proof that stable stationary points of linear density constraints occur only at energy maxima with respect to their Lagrange multipliers. We show that multiple solutions, hysteresis, and energy discontinuities may occur in cDFT. Expressions are derived, in terms of convenient by-products of cDFT optimization, for quantities such as the dielectric function and a condition number quantifying ill-definition in multi-constraint cDFT.

1. README for the data catalogue

This archive contains open-data for Optimization of constrained density functional theory " by David D. O'Regan and Gilberto Teobaldi, accepted for publication in Physical Review B

The open data is organized as follows:

- Figure*.agr: xmgrace files and raw data of the figures in the paper
- Figure*.txt: raw data of the figures in the paper

Description of the Methods used to generate the data follows in Section 2.

2. Methods

The ONETEP linear-scaling simulation code⁵⁷, was used to carry out cDFT calculations on the hydrogen molecule stretched to an internuclear distance of $3.2 a_0$, which, using the PBE functional⁵⁸ with no spin-orbit coupling, lies just beyond the Coulson-Fischer point at which an open-shell singlet ground-state becomes favoured^{59,60} (see Fig. 1). A constraint was placed on the difference of spin magnetic moments, ΔM , between the two hydrogen atoms, defined on the basis of their isolated 1s valence pseudo-orbitals. The constraint target was set to $\Delta M_c = 0 \mu_B$, and the Lagrange multiplier V_c was defined such that increasing its value increased the spin-dependent potential acting to decrease ΔM . It was found that the unpolarized, closed shell "CS" state is metastable, starting from which any non-zero value of V_c initiates a collapse to one of two symmetry-related, degenerate open-shell ground-states, "OS(-)" and "OS(+)" defined in the caption of Fig. 1.

In order to check the validity of our approach for analyzing functional interdependencies and derivatives, and to numerically illustrate our analytical findings, we performed a cDFT study on the nitrogen molecule shown in Fig. 2. This serves to illustrate a case in which, if the constraint energy E_c vanishes for a finite Lagrange multiplier V_c , the total-energy W achieves a maximum with respect to V_c . The total and constraint energies W and E_c exhibit different negative curvatures, and their the difference, the DFT component EDFT, necessarily exhibits a positive curvature around the ground-state minimum at $V_c = 0$ eV. For each value of the charge-constraining Lagrange multiplier, well converged BLYP^{67,68} ground-state energies and densities, with pseudized 1s states, were calculated using the ONETEP linear-scaling Kohn-Sham DFT code⁵⁷. This code solves for the ground-state by optimising a minimal set of nonorthogonal generalized Wannier functions⁶⁹ in situ. Each of these functions is expanded in an underlying variational plane-wave equivalent basis set and truncated within a prescribed cut-off sphere, in this particular case to a radius of $10 a_0$. This approach has been shown to offer finite-difference linear response properties with an accuracy matching that of conventional plane-wave DFT⁷⁰. The constrained population was defined using the four 2s and 2p valence pseudo-orbitals of the isolated atom⁷¹. In the dimer, the resulting unconstrained ground state atomic occupancy was approximately 6:5 e, due to overlap between pseudo-orbitals. The charge of one of the nitrogen atoms was constrained, with the target occupancy set to $N_c = 6:0$ e.

References

57. C.-K. Skylaris, P. D. Haynes, A. A. Mostofi, and M. C. Payne, The Journal of Chemical Physics 122, 084119 (2005).
58. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).

59. C. Coulson and I. Fischer, *Philos. Mag.* 40, 386 (1949).
60. A. Ruzsinszky, J. P. Perdew, and G. I. Csonka, *The Journal of Physical Chemistry A* 109, 11006 (2005).
67. A. D. Becke, *Phys. Rev. A* 38, 3098 (1988).
68. C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* 37, 785 (1988).
69. C.-K. Skylaris, A. A. Mosto_, P. D. Haynes, O. Di_eguez, and M. C. Payne, *Phys. Rev. B* 66, 035119 (2002).
71. The resulting constraint acts on the Kohn-Sham density matrix rather than on the density. Our analytical findings extends to that case with minor notational changes.