

Development of a code for optimally tuned range-separated density functional calculations

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It has been suggested that the performance in predicting fundamental and optical gaps of range-separated functionals (RSH) in DFT calculations can be improved by tuning the range-separation parameter, γ , in order to actively enforce Koopman's theorem, which states the eigenvalue of the HOMO is equal to the ionisation energy of the system, $\varepsilon_H = I$. Enforcing Koopman's theorem for both the N and N+1 system provides the following cost function that when minimised provides a optimal value of $\gamma^{1,2,3}$

$$J^2(\gamma) = (\varepsilon_{H(N)}^\gamma + I^\gamma(N))^2 + (\varepsilon_{H(N+1)}^\gamma + I^\gamma(N+1))^2 \quad (1)$$

In order to develop an algorithm that will minimise the cost function, first the behaviour of the $J^2(\gamma)$ function needed to be understood. A set of simple, organic, reference molecules with a literature set of OT-RSH calculations¹ were selected in order to develop the code. Initially, a grid method was employed. First, an array of γ values at low resolution were submitted between $0.0 \leq \gamma \leq 0.5$. The area around the value of γ with the lowest value of $J^2(\gamma)$ was then investigated further at higher resolution. This process was then repeated again and determined the optimal value of γ , γ_{opt} , to three decimal places. (See Fig. 1)

Once the behaviour of the $J^2(\gamma)$ had been understood, it became apparent that the minimum of the function could be found by fitting a polynomial to a set of data points.

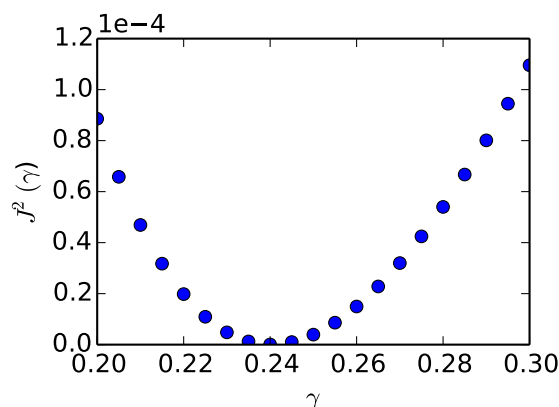


Figure 1: Plots showing the behaviour of the $J^2(\gamma)$ function around the minimum for the reference set molecule fluorene

Attempts at fitting the a polynomial to sets of data points showed that the value of γ_{opt} could be predicted by fitting a 4th-order polynomial to 5 data points within ± 0.05 of the γ_{opt} . This finding was then applied to the development of a 3-part code that was shown to be successful at finding γ_{opt} values for the reference set of molecules selected, and also for providing accurate predictions of fundamental and optical gaps.

Once the code had been developed and was shown to be reliable, it was then ready to be applied to a variety of systems. Fundamental and optical gaps of solvated systems are of particular interest in the fields of photo-catalysis and photo-voltaics. In order to simulate the effect of a solvent, COSMO, a form of conductor-like polarisable continuum model (c-PCM) was ap-

plied.^{4,5} In c-PCM the solvent is considered to be a homogeneous medium with dielectric constant ϵ_r interacting with a smooth cavity encapsulating the molecule. Fundamental and optical gaps were determined in a non-polar organic ($\epsilon_r = 2.0$, and water ($\epsilon_r = 80.1$). For both, two sets of γ_{opt} were used, one optimised in the solvent and one in vacuum. Results showed that the use of γ_{opt} from the vacuum in some cases caused the fundamental gap to increase, a result does not make physical sense, and thus the method is likely unreliable. Optimisation of γ in the solvent lead to low fundamental gaps and γ_{opt} values. It has been shown in the literature that these values are artificially low and that to apply the OT-RSH methodology to solvated molecules co-ordination shells must be considered on an individual molecule basis.^{6,7}

After this the OT-RSH approach was applied to a selection of small titanium dioxide clusters ($Ti_n, n \leq 4$), as well as a two hydrated clusters. Fundamental gap calculations were shown to be in reasonable agreement with $qsGW$, although they did not entirely match the trends seen from cluster to cluster.⁸ Analysis of this showed that the for the two clusters that did not fit the trend shown by $qsGW$ and G_0W_0 , the optimal γ values for enforcing Koopman's theorem for the N and N+1 systems were too far apart, leading an γ_{opt} that did not sufficiently enforce Koopman's theorem for either system, resulting in an overestimation of the fundamental gap.(see Fig. 2) For the molecules that this was not the case the fundamental gaps were close to those given by $qsGW$.

Examination of optical gaps for the titanium

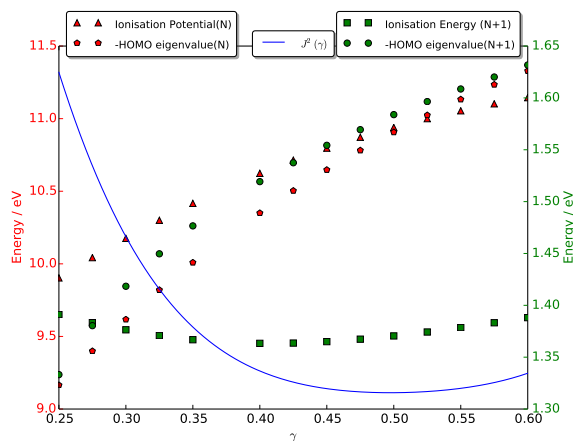


Figure 2: Plots of ionisation potentials and HOMO eigenvalues for the N and N+1-electron systems as a function of γ calculated using OT-BNL for *cis* – (TiO_2)₂. The large gap in γ values were the ionisation potential and HOMO eigenvalue is the same for different systems causes the method to breakdown

dioxide clusters showed that the OT-RSH approach performed better than B3LYP, but not as well as CAM-B3LYP with respect to EOM-CC. It did not show the reduction in optical gap found in charge-transfer like excitations that B3LYP exhibits, thanks to the asymptotic decay of the exchange correlation. The accuracy of determination of the optical gap in OT-RSH is directly related to the accuracy of the fundamental gap, and the molecules for which the fundamental gap was not in agreement with $qsGW$, there was also little agreement with the optical gaps found using EOM-CC.⁹

References

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