

Reply to Reviewers' queries:

Excited states forces with GW-BSE through the Hellmann-Feynman theorem

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Response to Reviewer: 1

This manuscript proposes an interesting approach to compute excited-state forces within the GW-BSE approach. GW-BSE is a state-of-the-art approach to compute the excited-state properties of complex systems. However, computing forces within it is still a challenging task. The work in this manuscript is a valuable try on this direction. Comparison with other theoretical approaches and experiments support the validity of this new approach. Followings are some comments which the authors should consider before the manuscript can be accepted for publication.

We are grateful to the Reviewer for having acknowledged the merits and the validity of our work.

(1) Figure 2 contains four kinds of colors, but the authors only give explanations to three of them. What does the blue one represent? The blue dotted line and the yellow dotted line represent the accurate brute forces calculated by the numerical differentiations of excited state energies. According to Figure A1, the excited state energy curves between 1.9 and 2.3 Bohr for all the states are very smooth, so their corresponding brute forces in this internuclear separation range should vary smoothly. But the blue dotted line and the yellow dotted line in Figure 2 are not smooth between 1.9 and 2.2 Bohr. The authors attribute this phenomenon to level crossing. The lowest excited state (green line in Figure 1) also has crossings with other two states between 2.3 and 2.6 Bohr. Why is the green dotted line in Figure 2 smooth? Even if there are level crossings, the accurate forces should be smooth. Why do all the dashed lines are smooth? All in all, the blue dotted line and the yellow dotted line are unphysical. There must be some problem in the approach to compute the accurate brute force.

We apologize for the mismatch of colors in Fig. 2: yellow and orange were meant to be the same color as well as blue and bluet. We have now corrected the error choosing 'red' for the ground state and 'blue', 'green' and 'orange' for the three excited states of CO. The 'brute force' forces in Figure 2 were calculated simply by taking finite differences of total energies of excitons at the same order. For example, the energy of the 2nd exciton for a bond length of 2.0 Bohr minus the energy of the 2nd exciton for a bond length of 1.8 Bohr. Unfortunately, as can be seen from Figure A1, at short C-O distances there is plenty of level crossing so that the same

exciton is found at different levels. For example, the 2nd exciton could go into the 5th. While our new approach is insensitive of this, the brute force approach is not. More excitons must be evaluated together with the respective overlaps. We proceeded in this way and now in the new Fig 2 all forces are smooth. We note that for calculating the forces of Fig 2 at 1.9 Bohr we had to increase the number of excited states from 10 to 20 in order to cope with level crossing. In the manuscript we have: updated Fig 2 with the correct (smooth) forces, updated Figure A1 plotting 20 excitons and connecting with dashed lines corresponding excitons, added a sentence in the text for explaining that even for a so small system level crossing is an issue when using 'brute force' derivation.

(2) On page 2, it is written that 'Compared to finite differences, the use of this Hellmann–Feynman scheme requires only one BSE calculation.' The most difficult and time-consuming part of a BSE calculation is constructing the BSE Hamiltonian H^{exc} . According to Eqs. (30) and (31), $H^{exc}(\Delta\lambda)$ and $H^{exc}(-\Delta\lambda)$ also need to be calculated. Taking into account $H^{exc}(\Delta\lambda = 0)$, that implies three BSE calculations if I understand correctly. If not, the manuscript should describe how $H^{exc}(\Delta\lambda)$ is computed.

The Reviewer is correct. With our approach we avoid $6N$ diagonalizations of the BSE Hamiltonian while $6N$ constuctions of the exciton Hamiltonian are required.

(3) If I understand correctly, the value of the term $(1 + g(\Delta\lambda)^2 - g(-\Delta\lambda)^2)$ in Eq. (32) is close to one. So $\frac{1}{2\Delta\lambda}(1 + g(\Delta\lambda)^2 - g(-\Delta\lambda)^2)$ would be a very large value. Is it reasonable to follow it by $\frac{\partial E_0}{\partial \lambda}$

Unfortunately, the pre-factor $\frac{1}{2\Delta\lambda}$ was a typo. We apologize for this. We have also noticed that in the linear regime $g(\Delta\lambda) = -g(-\Delta\lambda)$ so that we can simply add the ground state force. We have corrected the formula in the equation and we have added in the text a sentence for explanation.

(4) The unit in the manuscript should be consistent. For example, in Table 1 and the context the unit of energy is eV, but in Figure 1/2/A1 the unit of energy is Ry.

In the manuscript we opted for Ry units when referring to total energies of the molecule and to eV when referring to (single) excitation energies. This choice stems from the customary use of Ry/Bohr as the unit for atomic forces and from the common use of eV for excitations. We would prefer to maintain this choice if it were in accord with guidelines of IJMS.

(5) In Figure 2, the force in the green dashed line becomes zero when the bond length is about 2.45 Bohr, but Table 2 gives a value of 2.40 Bohr. The two values of 2.56 Bohr are inconsistent with Figure 2 as well. These should be corrected.

We have now corrected the figures. The previous ones were from an older calculation with not optimized parameters. We are grateful to the Reviewer for having noticed this.

(6) In the discussion on formaldehyde, potential curves like those in Figure 1 should be provided to support the data in Table 3.

Thank you for the insightful comment. We have added a figure in the Supporting Information

displaying the energy surfaces of formaldehyde in its first excited state. We have also added a sentence in the main text referring to such material.

(7) There is one error on page 8 in the citing of reference.

Thank you for pointing this out. We fixed it in the manuscript.