Illuminating a better way to calculate excitation energy

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Glow sticks, like those brandished by trick-or-treaters and partygoers, light up due to excited electrons of the molecules in the contained fluorescent dye. Electrons accept the exciting energy from a chemical reaction that results when an inner tube in the glow stick is cracked and two fluids come into contact. After exciting to a higher energy level, they relax back to a lower energy by releasing light that can guide young candy hunters in costumes.

A glow stick's color offers a direct way to visualize excitation energy, the energy required to send a single electron into an excited state. But this phenomenon plays fundamentally important roles in numerous situations, such as charging a cell phone, imaging cells with fluorescent microscopy and photosynthesis in plants. Researchers in multiple fields rely on understanding excitation energies of materials in their work, but calculating their values is notoriously difficult and becomes incredibly complex for electrons in larger compounds and polymers.

In a new study appearing this week in the *Journal of Chemical Physics*, researchers at Temple University demonstrate a new method to calculate excitation energies. They used a new approach based on density functional methods, which use an atom-by-atom approach to calculate electronic interactions. By analyzing a benchmark set of small molecules and oligomers, their functional produced more accurate estimates of excitation energy compared to other commonly used density functionals, while requiring less computing power.

The density functional has widespread potential for use due to its improved accuracy and because it is a non-empirical functional, meaning that it does not rely on data from specific conditions in the calculation. Thus, it can be universally applied to address questions in chemistry, physics and materials science.

"We tried to develop a new method that is good not only for the ground (lowest energy) state, but also for the excited state. We found that because this method gives a very good estimate of excitation energy, it can be further applied to study other dynamical properties," said Jianmin Tao, research assistant professor of physics at Temple University. "This functional may provide novel insights into excitation energy or related properties of molecules and materials."

The functional is especially efficient in terms of computing power because it is semi-local, and uses the electron density at a reference point, as well as information around the reference point to inform the calculation. Like other semi-local functionals, however, the new method has room for improvement in calculating excitation energies for conjugated oligomers—compounds composed of multiple units containing alternating single and multiple bonds, which share delocalized electrons.

In future work, Tao plans to apply the functional to study luminescent and fluorescent dyes, which absorb and emit light of particular measurable wavelengths. These molecules are invaluable for biomedical research, where they can be used to tag specific cells or proteins under the microscope, or in diagnostic tests to detect particular DNA sequences. Estimating the excitation energies of these complex materials, however, is a computationally heavy task.

"Dyes are usually large, conjugated oligomers and polymers," explained Tao. "Their optical spectra can be fine-tuned by manipulation of the

molecule's skeleton, so this functional should be very useful in the design of light-emitting materials, due to its high computational efficiency and good accuracy," Tao said.

More information: Guocai Tian et al, Accurate excitation energies of molecules and oligomers from a semilocal density functional, *The Journal of Chemical Physics* (2017). DOI: 10.1063/1.4984062

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