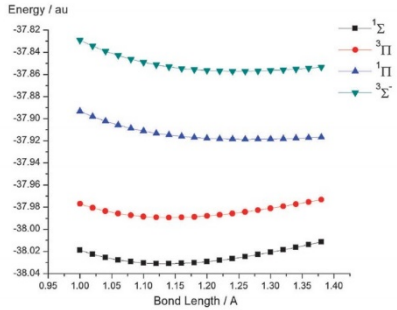
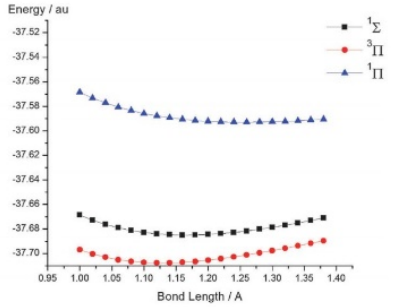
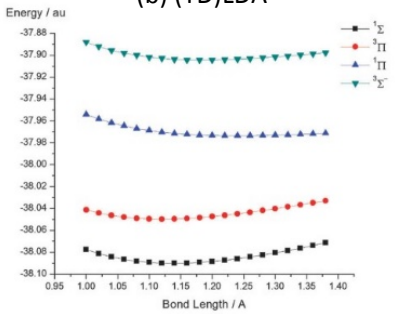
Potential energy surfaces and analytic gradients from pp-RPA for electronic excitations



(a) Full CI



(b) (TD)LDA



(c) pp-RPA with B3LYP reference

Scientific Achievement

Derived and developed the energy gradients for particle-particle random phase approximation (pp-RPA) to ground state and excitation energy and studied the ground state and excited state potential energy surfaces by double-electron addition to an (N-2)-particle reference system described by DFT.

Significance and Impact

Excited state potential energy surfaces are of great significance in the design of solar cells, and other areas of chemistry, biology, and materials science. This work allows the study of dynamics on ground-state and excited-state energy surfaces using the same theory, going significantly beyond the accuracy of current DFT and TDDFT.

Research Details

–The analytic gradient for the pp-RPA excitation equation has been developed and the geometry optimization implemented, in a similar manner to that of TDDFT excitation energy.

–The pp-RPA calculation of ground state and excited state potential energy surfaces and molecular structures for the *N*-particle systems have been performed to address major challenges of TDDFT, e.g. double excitations, singlet-to-triplet instability and bond dissociation. With a similar structure of equation to that of TDDFT, pp-RPA can overcome the above challenges without significantly increasing the computational cost.

–The figures on the left illustrate that the pp-RPA potential energy surfaces (in (c)) for CH^+ rectify the qualitatively wrong description of TDLDA (in (b)). pp-RPA not only corrects the wrong energy ordering in TDLDA for the ground state ($^1\Sigma$) and the lowest triplet excited state ($^3\Pi$) but also captures the low-lying doubly excited state ($^3\Sigma^-$) that is missing completely from the adiabatic TDDFT. The pp-RPA potential surfaces agree well with the Full CI benchmark results (in (a)).

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Work was performed at Duke University

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