A New TDDFT Method for Optical Design of Metal Clusters

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A new algorithm to solve the TDDFT equations in the space of the density fitting auxiliary basis set has been developed and implemented [1]. The method extracts the spectrum from the imaginary part of the polarizability at any given photon energy, avoiding the bottleneck of Davidson diagonalization. The original idea which made the present scheme very efficient consists in the simplification of the double sum over occupied-virtual pairs in the definition of the dielectric susceptibility, which allows an easy calculation of such matrix as a linear combination of constant matrices with photon energy dependent coefficients. The method has been applied to very different systems in nature and size (from H_2 to $[Au_{309}]^{3+}$). In all cases, the maximum deviations found for the excitation energies with respect to the Amsterdam Density Functional code are below 0.2 eV. The new algorithm has the merit to calculate the spectrum at whichever photon energy but also to allow a deep analysis of the results, in terms of Transition Contribution Maps [2], plasmon scaling factor analysis [3] and induced density analysis, which have been all implemented. Recent applications to large bare Au and Ag clusters will be shown, as well as new results on the implementation of the rotatory strength (R) in order to study dichroism in large chiral clusters.

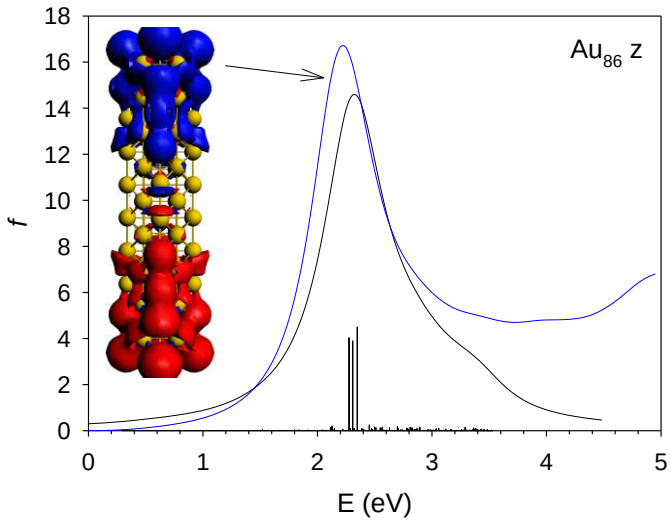

Figure 1: Transversal plasmon in Au_{86} nanowire [4].

References

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