A new implementation of dynamic polarizability evaluation using a multi-resolution multi-wavelet basis set

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Abstract. An algorithm to evaluate the response function on the space spanned by Multi-resolution Multi-wavelet (MRMW) basis functions is implemented in a new efficient quantum chemical program system. Dynamic electric dipole polarizability of a molecule is evaluated for a range of applied optical frequencies as a preliminary application of the implementation. The results obtained by the MRMW provide the one in near completeness limit. We also compare a few examples of the dynamic polarizabilities evaluated using conventional Gaussian basis set functions with the one evaluated by the MMMW basis functions. For small frequencies, there is no significant difference among them and large Gaussian results are close to the MRMW value, but they diverge from the MRMW value when the applied frequency approaches to the resonance region.

1. Introduction

Electric polarization of matter caused by optical field provide a variety of interesting properties in materials and the response of the electrons against the electro-optical perturbation in the consisting molecules is responsible for the electric polarization of the matter. Quantitative evaluation of the polarization needs quantum mechanics on the electrons in molecules. While interactions among electrons and electron with nuclei are important in the quantitative evaluation of the polarizability, precision of the model space to which infinite dimensional Hilbert space is truncated is another very important issue. We have developed an algorithm for computing response functions such as electronic polarizability as well as electronic wavefunction using Multi-resolution Multi-wavelet (MRMW) basis function. The results by the preliminary program written in Python provided the evaluation of static polarizabilities for a series of small molecules in near basis set limit. While the results computed indicated the algorithm to be superior over conventional Gaussian basis set technology, the computational resources such as storage space required for the MRMW algorithm is more demanding. New implementation in the program based on new massively parallel environments has been awaited. We implement an algorithm for evaluating dynamic polarizability in the quantum chemical electronic structure program MADNESS. While static polarizabilities and hyperpolarizabilities are very important index for some materials designing where fast off-resonance
response upon optical exposure to the molecules determines the functionality of the material qualitatively, dynamic polarizabilities are the one which should be compared with experiments. The latter is much more important especially for observations at near resonance region since the magnitude of the response is much more enhanced there. However the evaluation of dynamic polarizability involves more elaboration of the quantum chemical technology than that for static polarizability (frequency zero limit). We briefly discuss the theoretical framework of the evaluation of the dynamic polarizability on the near complete space spanned by the MRMW basis functions. We provide MRMW dynamic polarizability of hydrogen molecule computed for a range of applied frequencies and compare the one computed by the different Gaussian basis functions against the MRMW results.

2. Theoretical method
Polarizability is evaluated as a response coefficient of the dipole polarization which is defined by

$$\mu_\zeta(E_\zeta(\omega)) = \mu_\zeta^0 + \alpha_\zeta(\omega) \cdot E_\zeta(\omega) + \ldots$$

and is determined from the first-order density operators $\rho(+\omega)$, $\rho(-\omega)$

$$\alpha_\zeta(\omega) = -\text{Tr}(\zeta \cdot (\rho_\zeta(+\omega)))$$

$$\rho(\omega) = \rho^{(0)} + \rho(+\omega)\lambda e^{+\omega} + \rho(-\omega)\lambda e^{-\omega} + \ldots$$

Here $\rho^{(0)}$ is a zero-th order density operator.

The $p^{th}$ response function is defined as a set of parameter functions

$$u_p^{(+)} = (1 - \rho^0)\rho(+\omega)\rho_p^0$$

$$u_p^{(-)} = (1 - \rho^0)\rho(-\omega)\rho_p^0$$

to represent the first-order density operators. Here $\rho_p^0$ is the $p^{th}$ orbital contribution to the zero-th order density operator $\rho^0$ generated from the zero-th order orbitals. The equation of motion for the perturbed density operators can then conveniently expressed as the coupled equations with respect to $u_p^{(+)}$, $u_p^{(-)}$.

$$(F_0 u_p^{(+)} - u_p^{(+)} \varepsilon_p^0) + \left\{ \frac{d}{2} + \frac{\delta \xi}{\delta \rho} [\rho^0] \right\} \left( \sum_{i=1}^{N_{occ}} u_i^{(+) \phi_i^0} + \sum_{i=1}^{N_{occ}} u_i^{(-) \phi_i^0} \right) = \omega u_p^{(+)}$$

$$(F_0 u_p^{(-)} - u_p^{(-)} \varepsilon_p^0) + \left\{ \frac{d}{2} + \frac{\delta \xi}{\delta \rho} [\rho^0] \right\} \left( \sum_{i=1}^{N_{occ}} u_i^{(-) \phi_i^0} + \sum_{i=1}^{N_{occ}} u_i^{(+) \phi_i^0} \right) = -\omega u_p^{(-)}$$

Where $F_0$, $\phi_p^0$, $\varepsilon_p^0$, $d$ and $\frac{\delta g}{\delta \rho} [\rho]$ are zero-th order Hamiltonian, orbital, orbital energy, dipole operator and coulomb and exchange interactions for Hartree Fock (HF) and exchange-correlation functional for Density Functional Theory (DFT). A*B indicates the convolution of A and B. Note that no operator such as density operator is stored as an array and all the unknowns such as response functions are stored in one-dimensional arrays during the solution of the above equations.

Equations (5a) and (5b) are solved using Green’s function technique for the kinetic energy term with the free space boundary condition.

$$u_p^{(+)} = G(\omega) [V_0 u_p^{(+)} + \left\{ \frac{d}{2} + \frac{\delta \xi}{\delta \rho} [\rho^0] \right\} \left( \sum_{i=1}^{N_{occ}} u_i^{(+) \phi_i^0} + \sum_{i=1}^{N_{occ}} u_i^{(-) \phi_i^0} \right)]$$

$$u_p^{(-)} = G(-\omega) [V_0 u_p^{(-)} + \left\{ \frac{d}{2} + \frac{\delta \xi}{\delta \rho} [\rho^0] \right\} \left( \sum_{i=1}^{N_{occ}} u_i^{(-) \phi_i^0} + \sum_{i=1}^{N_{occ}} u_i^{(+) \phi_i^0} \right)]$$
Here \( G(\omega) \) is the Green’s function

\[
G(\omega) = \left[ \varepsilon_p^0 + \omega - \left( -\frac{1}{2} \nabla^2 \right) \right]^{-1}
\]

and depends on the applied frequency.

The straightforward iterative solution of (6a) and (6b) converges slowly and not efficient especially for frequencies of near resonance. We employ Krylov subspace algorithm in order to improve the efficiency.

3. Results and discussion

We compute the dynamic dipole polarizability of the hydrogen molecule for many different frequencies (from 0.365 to 0.46 a.u.). The longitudinal component of Hartree Fock polarizability is plotted along the different frequencies (Fig. 1). The residual \( \varepsilon = 1 \times 10^{-4} \) and the order of polynomial \( k=6 \) are set for all the calculations. The values computed using conventional Gaussian function are plotted together. We also plot the deviation of the Gaussian results from the one obtained by the MRMW in Fig. 2. For the off-resonance region, all the results obtained by Gaussian basis sets are almost identical and coincides with the one by the MRMW except for relatively small Gaussian basis sets such as aug-cc-pVDZ and d-aug-cc-pVDZ. However, we observe the divergence of those values from the MRMW value in near resonance region even for larger basis sets. It seems that the addition of d-function to the large basis sets overshoots the MRMW value whereas enlargement of the basis by splitting valence area improves the Gaussian results towards the MRMW one. However, there is no definite criterion on the systematic improvement of the predicted polarizability as in the MRMW case. Intuitive construction by addition of extra functions to large Gaussian basis sets sometimes causes serious problems such as incapability of convergence because of over-completeness and the resulting overwhelming computational time. The MRMW basis functions are completely local and no issue relating to over-completeness arises. Systematic and guaranteed improvement of the space is expected by only setting a threshold for the residuals of the target property.

Fig. 1
4. Conclusion
A code based on the response function algorithm is implemented in MADNESS which is a framework for scientific simulation in many dimensions using adaptive multi-resolution methods in multi-wavelet bases. The preliminary application for the evaluation of dynamic polarizability shows potential problems of Gaussian as incomplete basis set in the near resonance region.

While we have already shown the strength of the MRMW algorithm in quantum chemical computation a while ago, the memory handling issue arising from the huge number of polynomials representing the quantum properties such as wavefunction and response functions with sufficient precision was problematic for older generation of scientific computational environments. The situation is rapidly being altered because of the availability of inexpensive processors and memories with high quality. MADNESS is an object-oriented designed program and is created from the beginning as a parallel processing program for computers with up to millions of cores running on the Cray XT5 at Oak Ridge National Laboratory and the IBM Laboratory and the IBM Blue Gene at Argonne National Laboratory. We expect the new implementation will enable us to evaluate interesting properties such as dynamic polarizability and hyperpolarizabilities of larger molecules at near resonance with high precision.

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