Quantum Computational Ab-initio Methods with Different Perturbation Theories and their Application to Nonlinear Optical Material Investigations

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Abstract: *The search of a novel non linear optical material is usually done by intelligent assumption and synthesis feasibility. Computational chemistry techniques play important role during investigations of such materials and can provide experimentalists with precise information regarding the properties and behavior of materials. These techniques can help resolve issues that cannot be practically achieved due to instrumentation limits. It also helps the researcher to know about the chemical systems before performing the actual experiments. A wide variety of methods such as molecular mechanics methods, semi empirical methods and ab-initio methods are generally used in computational chemistry for calculating molecular properties. Out of which the ab-initio quantum chemistry method has turned into a fundamental tool in the investigation of atoms and molecules. The purpose of the present paper is to outline approach and easiness of the ab-initio theories to the quantum calculations in search of novel nonlinear optical materials.*

Keywords: Quantum chemistry, Spectroscopy, Nonlinear optics, NLO, NLO materials, SHG, frequency doubling, DFT, Ab-initio methods, Molecular mechanics, SCF

1. Introduction

Now days, methods in computational chemistry have become a key to investigate nonlinear optical materials which are very far away from our reach. It also helps the researcher to know about the chemical systems before performing the actual experiments. The quantum mechanics, classical mechanics as well as statistical physics and thermodynamics are the foundation bricks for most of the computational chemistry theory and the software associated with it. All important methods which are used in computational chemistry for calculating molecular properties and processes may broadly be divided in to three categories. [1-3]

1) Ab-initio methods-which uses Schrödinger's equation, but with approximations,
2) Semi-empirical methods - using experimental parameters and extensive simplifications of Schrödinger's equation
3) Molecular mechanics methods -is a classical approach which deals with bonds between the atoms in a molecule.

Ab-initio methods
Over the past few decades, the ab-initio quantum chemistry has turned into a fundamental tool in the investigation of atoms and molecules. The approximations made are generally mathematical approximations using a simple functional form for a function or wave function. The core technology behind this is getting a computational approximate solution for Schrodinger equation describing the positions of a collection of atomic nuclei and the total number of electrons in the system and then to calculate the electronic energy, electron density and other properties by means of a well defined automated approximation.

Generally, ab-initio calculations produce very good qualitative results and the advantage of this method is that they ultimately converge to the near accurate solution, once all the approximations are included properly [4].

A wide variety of methods are implemented in the computer programs to approximate wave functions, which are the solutions to complex wave equations. These molecular wave functions carry the information about all the electrons, spatial as well as spin coordinates. The wave function is calculated quantum mechanically by solving the non-relativistic Schrodinger wave equation. Most of these methods are developed on the basis of one-electron model in which electrons move independently under the influence of average potential of other electrons, nuclei, and external fields (Hartree Fock method). These one-electron wave functions constitute atomic orbitals. Since the molecule of any substance is made up of atoms, so a very effective method has been developed to expand the molecular orbitals in the form of centered atomic orbitals [5-6].

These methods can be further classified into two classes. The first one is post-Hartree Fock schemes in the framework of configuration interaction or coupled cluster methods which are based on wave-function and can be used for molecules containing up to a few tens of atoms and are likely to provide precise results. The second one is electron density based density functional theory (DFT) which may be employed over the systems containing a few tens up to a few hundreds of atoms [7-9]. DFT provides the wide-range of applicability and reasonably accurate results in many cases. The classification of different types of ab-initio methods can be better understood using Figure 1.
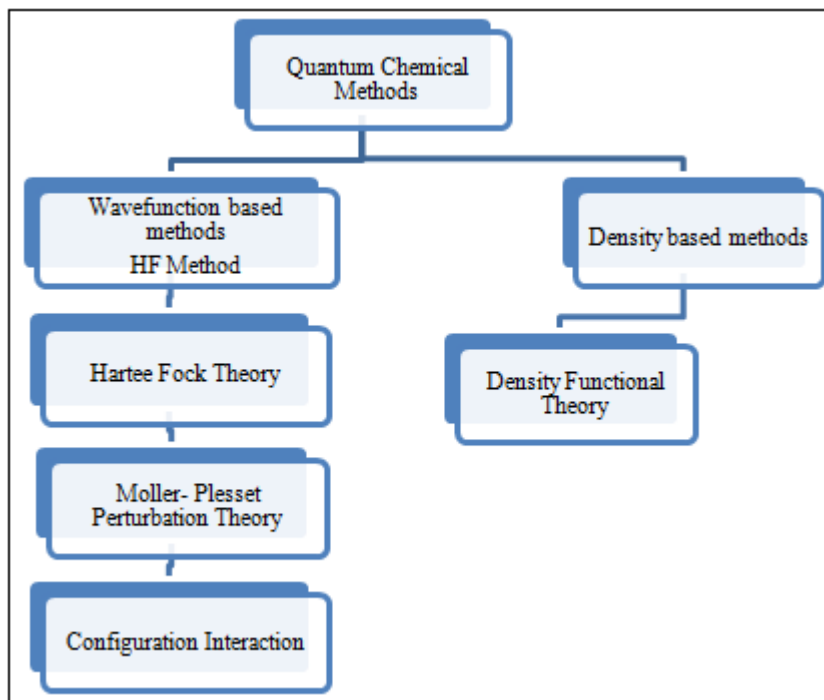
Figure 1

In DFT, the total energy is expressed in terms of electron density functional, rather than the wave-function. This type of calculation leads to an approximate effective or model Hamiltonian and to an approximate expression for the total electron density. Three types of DFT calculations exist:

- Local density approximation (LDA) – fastest method, gives less accurate geometry, but provides good band structures.
- Gradient corrected - gives more accurate geometries.
- Hybrids (which are a combination of DFT and HF methods) - give more accurate geometries.

Electronic Structure Calculations
The main objective of any theory of molecular structure is to provide some insight into chemical constitution of molecules in terms of the more fundamental universal physical laws governing the motions and interactions of the constituent atomic nuclei and electrons. In principle such theories can aim at a precise quantitative description of the structure of molecules and their chemical properties, since the underlying physical laws are now well understood in terms

of quantum theory based on Schrödinger equation. However, in practice mathematical and computational complexities make this goal difficult to attain, and one must usually resort to approximate methods [10].

While energy is undoubtedly the fundamental quantity, we often characterize molecules and their behavior by other properties. We might think of properties such as the dipole moment and polarizability that characterize features of the molecular charge distribution and those that characterize the structure, such as molecular geometry and vibrational frequencies, electronic transitions and time dependent qualities. The properties of any (non-relativistic) time-independent quantum system can be determined by solving the Schrödinger equation [11],

$$H\,\Phi(\{r_i\};\{R_A\}) = E\,\Phi(\{r_i\};\{R_A\}) \qquad \dots(1)$$

Where H is the Hamiltonian operator for a system of nuclei and electrons described by position vectors R_A and r_i, respectively. If there are N nuclei and n electrons, the many-particle Hamiltonian operator H is

$$\hat{H} = -\frac{\eta^2}{2}\sum_{A=1}^{M}\frac{1}{M_A}\nabla_A^2 - \frac{\eta^2}{2m_e}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A e^2}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{e^2}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B e^2}{R_{AB}} \qquad \dots(2)$$

Here M_A is the mass of nucleus A; m and e are the electronic mass and charge, respectively; $Z_A e$ is the charge on nucleus A; and r_{ij} is the distance between particles i and j. Summation involving indices A and B are over atomic nuclei and those involving i and j are over electrons. The first term in the equation is the operator for the kinetic energy of the electrons; the second term is the operator for kinetic energy of nuclei; the third term represents the coulomb attraction between electrons and nuclei; the fourth and fifth terms represent the repulsion between electrons and between nuclei, respectively.

The complete treatment of a quantum-mechanical problem involving electronic structure is equivalent to the complete solution of the appropriate Schrödinger equation. A direct approach in terms of a mathematical treatment of the partial differational equation is practicable only for one particle systems. If there are N nuclei, there are 3N coordinates that define the geometry. Since several parameters are involved in large molecular systems, an exact solution of the Schrödinger equation for such large systems (many body problems) is impossible to achieve. Therefore, calculations of large molecules are done using electronic structure

techniques that employ approximations at various levels and further the molecular properties are evaluated by the use of numerical methods.

Ab-initio (or first principles) is a very useful technique to calculate various properties of many-electron systems accurately. Such type of calculations uses the correct Hamiltonian and does not use experimental data other than the values of fundamental physical constants. A Hartree-Fock Self Consistent Field (SCF) calculation uses the anti-symmetrized product of one electron functions that minimizes $\int \phi^* \hat{H} \phi d\tau$, where $\hat{H}$ is the true Hamiltonian. The Born-Oppenheimer approximation is the first stage of any quantum chemical calculation.

So in practice, rather than attempt to find a wavefunction describing both electronic and nuclear motion together, it is usually sufficient to break the problem into two parts and the motion of electrons in the field of stationary nuclei will be considered primarily. There is then a separate, purely electronic problem for each set of nuclear positions. This is a reasonable procedure because the masses of the nuclei are several thousand times larger than the masses of the electrons, so that the nuclei move slowly, and it may reasonably suppose the electrons to adjust themselves to new nuclear positions. This simplification is referred to as the Born-Oppenheimer approximation [12].

In more quantitative terms, the Born-Oppenheimer approximation amounts to separating off the nuclear kinetic energy and nuclear repulsion terms from H, and considering only the part of the Hamiltonian which depends on the positions but not the momenta of the nuclei. This is the electronic Hamiltonian operator H_{el}.

$$H_{el} = -\frac{\eta^2}{2m_e}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A e^2}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{e^2}{r_{ij}} \quad .. (3)$$

The solution to a Schrödinger equation involving the electronic Hamiltonian,

$$H_{el}\Phi_{el} = E_{el}\Phi_{el} \quad\quad .....(4)$$

is the electronic wave function,

$$\Phi_{el} = \Phi_{el}(\{r_i\};\{R_A\}) \quad\quad .....(5)$$

Which describes the motion of the electrons and explicitly depends on the electronic coordinates but depends parametrically on the nuclear coordinates, as does the electronic energy,

$$E_{el} = E_{el}(\{R_A\}) \quad\quad .....(6)$$

By a parametric dependence we mean that, for different arrangements of the nuclei, Φ_{el} is a different function of the electronic coordinates. The nuclear coordinates do not appear explicitly in Φ_{el}. The total energy for fixed nuclei must also include constant nuclear repulsion.

$$E_{tot} = E_{el} + V_{NN} \quad\quad .....(7)$$

Where

$$V_{NN} = \sum_{A}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}} \quad\quad .....(8)$$

Since, the electrons move much faster than nuclei, they keep adjusting to any change in the nuclei. Thus, as the nuclei move, the electronic energy varies smoothly as function of the parameters defining the nuclear configuration. Hence,

the Schrödinger equation for nuclear motion in the average field of the electrons is

$$H_N\Phi_N = E\Phi_N \quad\quad .....(9)$$

$$H_N = -\frac{\eta^2}{2}\sum_{A=1}^{M}\frac{1}{M_A}\nabla_A^2 + E_{tot}(\{R_A\}) \quad .....(10)$$

This equation describes the vibration, rotation and translation of a molecule, $\Phi_N = \Phi_N(\{R_A\})$ and E.. This approximation indicate that the true molecular wave function is

$$\Phi(\{r_i\};\{R_A\}) = \Phi_{el}(\{r_i\};\{R_A\}).\Phi_N(\{R_A\}) \quad.....(11)$$

In the Born-Oppenheimer picture the nuclei move on a potential energy surface (PES) which is a solution to the electronic Schrödinger equation.

Self-consistent field theory

The electronic Schrödinger equation (in atomic units):

$$\left[-\frac{1}{2}\sum_i \nabla_i - \sum_{i,A}\frac{Z_A}{r_{iA}} + \sum_{B>A}\frac{Z_A Z_B}{R_{AB}} + \sum_{j>i}\frac{1}{r_{ij}}\right]\Phi_{el}(r;R) =$$

$$E_{el}\Phi_{el}(r;R) \quad ..(12)$$

Or, in a more compact form

$[T_e(r) + V_{eN}(r;R) + V_{NN}(R) + V_{ee}]\Phi_{el}(r;R) = E_{el}\Phi_{el}(r;R)$ .....(13)

with **r** denoting electronic and **R** denoting nuclear coordinates.

E_{el} (plus or minus $V_{NN}(R)$), gives the potential energy experienced by the nuclei. $E_{el}(R)$ gives the PES from which the equilibrium geometry and vibrational frequencies may be obtained. The electronic wave function $\Phi_{el}(r,R)$ contains lots of useful information about molecular properties such as dipole (and multipole) moments, and polarizability etc.

For many electron systems, the electron-electron repulsion comes into play, which must be neglected for separable solvable Hamiltonian. The total electronic wave functions $\Psi(r_1,r_2)$ describing the motions of the two electrons would just be the product of two hydrogen atom wave functions $\psi_H(r_1).\psi_H(r_2)$. Thus, the general wavefunction may be written as

$$\Psi_{HP}(r_1,r_2,\ldots,r_n) = \Phi_1(r_1)\Phi_2(r_2)\ldots\ldots\Phi_N(r_N) \quad.....(14)$$

which is the Hartree product (HP) [13].

Although this form is very convenient, it fails to satisfy the antisymmetric principle which states that a wavefunction describing fermions should be antisymmetric with respect to the interchange of any set of space-spin coordinates.

Hartree-Fock Equation

For symmetric energy expression, variational theorem may be used which states that the energy calculated from an approximation to the true wave function, will always greater than the true energy. Hence, a better approximate wave function may be obtained by varying their parameters until we minimize the energy. The Hartree-Fock equations are obtained by imposing the condition (at the minimum, the first derivative of the energy E is zero.) on the expression for the energy, subject to the constraint that the molecular

orbitals remain orthonormal. This type of constrained minimization problem can be tackled by the Lagrange's method of undetermined multipliers (ε_{ij}) used. After including the necessary terms like columbic interaction, effect of antisymmetry of the total wave function, the resultant Hartree-Fock equation becomes,

$$\left[H_{core}(x_1) + \sum_{j\neq i} J_i(x_1) - \sum_{j\neq i} K_j(x_1) \right] \chi_i(x_1) = \varepsilon_{ij}\chi_i(x_1)$$
$$\ldots\ldots (15)$$

Making use of the fact that

$$[J_i(x_1)-K_i(x_1)]\chi_i(x_1) = 0 \quad \ldots\ldots (16)$$

leads to the following form

$$\left[H^{core}(x_1) + \sum_{j} J_j(x_1) - K_j(x_1) \right] \chi_i(x_1) = \sum_{j} \varepsilon_{ij}\chi_j(x_1)$$
$$\ldots\ldots (17)$$

Or, more simply

$$f_i(x_1)\chi_i(x_1) = \sum_{j} \varepsilon_{ij}\chi_j(x_1) \quad \ldots\ldots (18)$$

Where f_i is called the Fock operator.

$$f_i(x_1) = H^{core}(x_1) + \sum_{j} \left\{ J_j(x_1) - K_j(x_1) \right\} \ldots\ldots (19)$$

For a closed shell system, the Fock operator has the following form

$$f_i(x_1) = H^{core}(x_1) + \sum_{j=1}^{N/2} \left\{ 2J_j(x_1) - K_j(x_1) \right\} \ldots (20)$$

Density Functional Theory

The conventional approach to quantum chemistry uses the wave function ψ as the central quantity. The reason is that once we know ψ (or good approximation to it) we have access to all information that can be known about this particular state of our target system (as in Hartree-Fock approximation approach). The wave function is a very complicated quantity that cannot be probed experimentally and that depends on 4N variables, three spatial and one spin variable for each of the N electrons. The electron density ($\rho(r)$) that depends only on the three spatial variables and a more simple quantity. The fact 'A knowledge of the ground state density of $\rho(r)$ for any electronic system (with or without interactions) uniquely determines the system' was proved by Hohenberg and Kohn and it provides the basic framework for modern density functional methods [14]

According to Hohenberg and Kohn (H-K) theorem, the total ground state energy and other properties of a system were uniquely defined by the electron density (the energy is a unique function of $\rho(r)$) and the true ground state electron density minimizes the energy functional. The H-K theorem gives proof of existence of such functional but there is no prescription to construct it. If it is known accurately, quantum chemical technique will be able to derive the molecular properties exactly. Till now, the exact form of energy functional is not known. It is necessary to use approximations regarding various parts of the functional which deals the kinetic energy, exchange and correlation energies of the system of electrons. The simplest approximation is the local density approximation (LDA) which leads to a Thomas-Fermi term for kinetic energy and the Dirac (actually Block proposed first term for the exchange energy [15-21]. The corresponding functional is called Thomas-Fermi- Dirac energy. The Thomas-Fermi-Dirac with improvements is the present density functional method, since all components of energy are expressed via density alone without using many particle wave functions. However wave functions cannot be completely neglected in molecular calculations and for accurate calculations they have to be used as a mapping step between the energy and density.

Local Density Approximation (LDA)

Several different schemes have developed for obtaining approximate forms for the functional for the exchange-correlation energy. In the local density approximation, it is

$$E_{XC} = \int \rho(r)\varepsilon_{XC}[\rho(r)]dr \quad \ldots\ldots(21)$$

Where $E_{XC}[\rho(r)]$ is the exchange-correlation energy per electron in a homogeneous electron gas of constant density .To account for the inhomogeneity in the electron density distribution in a real system, a non local correction involving the gradient of ρ is often added to the equation (21). This is known as the generalized gradient approximation (GGA).

Hybrid functionals

In the modern DFT schemes, a portion of the Hartree-Fock (HF) exchange energy (E_x) is mixed to the DFT exchange-correlational (E_{xc}) term by using the adiabatic connection method proposed by Becke [22-23], so as to eliminate self-interaction effect. These schemes, also known as hybrid HF-DFT methods, have remarkable accuracy in predicting various molecular properties. Thus in the present DFT scheme,

$$E_{XC}^{hybrid} = C_{HF} E_X^{HF} + C_{DFT} E_{XC}^{DFT}$$
$$\ldots\ldots (22)$$

where C's are constants. For example, the Becke-style three parameter functional theory may be defined by the expression

$$E_{XC}^{B3lYP} = E_X^{LSDA} + C_0(E_X^{HF} - E_X^{LSDA}) + C_X \Delta E_X^{B88} + E_C^{VWN3} + C_C(E_C^{LYP} - E_C^{VWN3}) \cdots (23)$$

Here parameter C_0 allows HF and DFT exchange. C_X allows inclusion of Becke's gradient correction to LSDA.

Moller-Plesset Theory

Perturbation theory (PT) provides another approach for the treatment of correlation energy. The basic idea of this method is to divide the total Hamiltonian of the system in two parts: a zeroth-order part, H_o, which has known Eigen functions and Eigen values, and a so-called perturbation V. The general formulation of the perturbation theory is known as Rayleigh-Schrodinger Perturbation. When the Fock operator is chosen as the unperturbed Hamiltonian, the method is called Moller-Plesset perturbation theory (MPn, where n indicates the order of correction). The MP2 method is the most commonly used methods in quantum chemistry treating electron correlation. Alternatively, the name Many-

Body Perturbation Theory (MBPT) can be used to emphasize the more general nature of the theory. The Coupled-Cluster method may also be considered as an MBPT method involving summation to infinite order.

- Computational demands are much less severe than for *ab initio* methods of similar quality, hence the method is applicable to much larger molecules. Time needed for DFT calculations scales as N^3 while *ab initio* calculations as e^N, where N is the number of atoms (Figure 2).
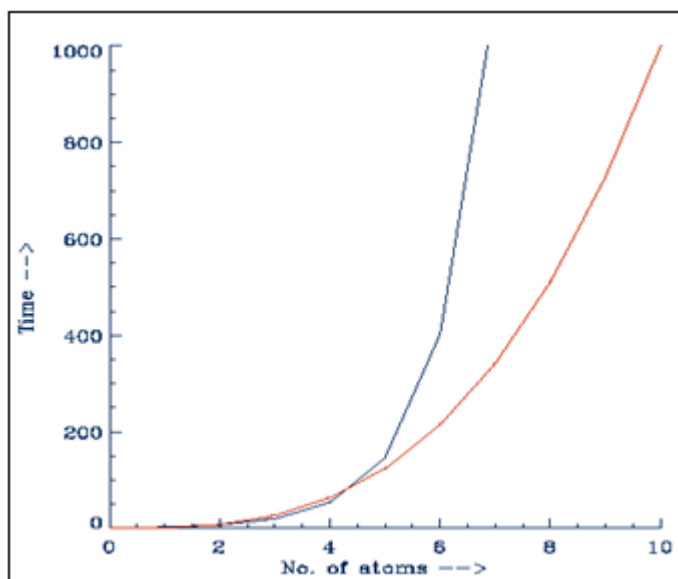
Advantages of DFT

Figure 2: Comparison of time taken for ab-initio (in blue) and DFT (in red) calculations

- *Ab initio* methods have severe problems with transition metals. In fact, it can be proved that Hartree-Fock equation cannot be solved for true metallic state. It is related to the fact that there is a difficulty to converge H-F when highest occupied orbitals are very close in energy (the situation typical for transition metals).
- The DFT, similar to *ab-initio* methods, is nonparametric, i.e., applicable to any molecule. Basis sets may not be assumed as parameters for *ab-initio* and DFT calculations as they are easily derived from atomic calculations.
- DFT method is applicable for the ground state only. This is not a problem unless complex studies such as interaction of radiation with biological molecules are being done using DFT calculations.

2. Conclusion

ab-initio calculations produce very good qualitative results and the advantage of this method is that they ultimately converge to the near accurate solution, once all the approximations are included properly. Such type of calculations uses the correct Hamiltonian and does not use experimental data other than the values of fundamental physical constants. The wave function is calculated quantum mechanically by solving the non-relativistic Schrodinger wave equation. Ab-initio methods can be further classified into two classes. The first one is post-Hartree Fock schemes in the framework of configuration interaction or coupled cluster methods which are based on wave-function and can be used for molecules containing up to a few tens of atoms and are likely to provide precise results. The second one is electron density based density functional theory (DFT) which may be employed over the systems containing a few tens up to a few hundreds of atoms. DFT provides the wide-range of applicability and reasonably accurate results in many cases.

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