

Density-functional theory of optical response

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In this paper we describe the perturbation theory developed recently by us within the time-dependent Kohn-Sham formalism for fields which are periodic in time. We demonstrate the $2n+1$ rule and its variational corollary for the time-averaged energy and employ it to calculate linear and various non-linear response properties of the inert gas atoms, helium, neon and argon.

Optical response¹ of a molecular system depends principally on the interaction of its electrons with an applied electromagnetic field. For normal field strengths, the response is described adequately by perturbation² theory. Thus the linear response properties such as the refractive index, as well as the non-linear properties which describe second harmonic generation, third harmonic generation, degenerate four-wave mixing, etc., are all calculated by applying perturbation methods. On the other hand, perturbation theory cannot be expected to describe properly the response of an electronic system to very intense fields that have become accessible lately. For such fields one must solve³ the Schrodinger equation exactly. In any case, to describe the response of a system to an optical field the starting point is the calculation of the electronic wavefunction, both without and with the applied field in the hamiltonian. This is where the theories of electronic structure enter the field of optics. In this paper we focus our attention on density-functional theory (DFT)^{4,5} of electronic structure and its application to calculate the optical response properties of an electronic system. We are concerned with the linear and nonlinear optical properties so that our approach is perturbative in nature. DFT can also be applied to study systems subjected to intense fields where the problem is solved in a nonperturbative manner. We are not going to discuss that here and refer the reader to the literature⁶⁻⁹. In what follows, we first briefly review, in Sec I, the basic tenets of time-dependent perturbation theory¹⁰ and variation-perturbation methods for applied fields which are periodic in time. This is done within the steady-state formalism of Sambe¹¹. We then discuss time-dependent DFT¹² in Sec II. In Sec III we describe our

work^{13,14} on the development of perturbation theory within the realm of time-dependent DFT, and in Sec IV, its applications^{14,15}. We conclude with a discussion of the direction for future research.

I. Perturbation theory and variation-perturbation method for time-dependent potentials

In this section we discuss the perturbative treatment of a system subjected to time-dependent potentials which are periodic in time within the steady-state formalism of Sambe¹¹. This formalism is based on the fact that the wavefunction $\Psi(\mathbf{r}, t)$ for a periodic hamiltonian with period T can be written in the form $\Psi(\mathbf{r}, t) = \Phi(\mathbf{r}, t)e^{-iEt}$, where $\Phi(\mathbf{r}, t)$ is also periodic with time period T and satisfies the equation

$$H - i(\partial/\partial t) \Phi(\mathbf{r}, t) = E \Phi(\mathbf{r}, t) \quad \dots(1)$$

The eigenvalue

$$E = (1/T) \int_0^T dt \langle \Phi | H - i(\partial/\partial t) | \Phi \rangle \quad \dots(2)$$

is a functional of Φ and can be shown, by using the Hellmann-Feynman theorem¹⁶ for time-dependent hamiltonians, to be the average energy of the system in a periodic field. It is thus referred to as the quasi-energy of the system. For example, if a polarizable system is in an electromagnetic field, E would represent the induction energy due to the interaction of the applied field and the induced polarization. Equation(1) above is similar to the stationary-state Schrodinger equation except

that the function $\Phi(\mathbf{r}, t)$ is now time-dependent. Also the operator $[H - i(\partial/\partial t)]$ is not hermitian in the Hilbert space $\mathbf{R}$ of square-integrable functions because of the time-derivative. However, Sambe proposed that one can treat Eq. (1) exactly like the stationary-state Schrodinger equation if the space $\mathbf{R}$ is extended. The extended space $(\mathbf{R} + \mathbf{T})$ consists of functions $u(\mathbf{r}, t)$ which are periodic in time with period T and for which

$$\int_0^T dt \int |u(\mathbf{r}, t)|^2 d\mathbf{r} \quad \dots(3)$$

Eq. (3) is finite. Further, the inner product of two functions $u(\mathbf{r}, t)$ and $v(\mathbf{r}, t)$ in this space is defined as

$$\{u|v\} = (1/T) \int_0^T dt \int u(\mathbf{r}, t)^* v(\mathbf{r}, t) d\mathbf{r} \quad \dots(4)$$

Note that with this inner product, the functions which are orthonormal in $\mathbf{R}$ also satisfy orthonormality in $(\mathbf{R} + \mathbf{T})$. Further, the operator $[H - i(\partial/\partial t)]$ now becomes hermitian in the extended space. As such we can now treat this operator as the hamiltonian in $(\mathbf{R} + \mathbf{T})$ space with the energy being given by Eq.(2). With these definitions Sambe showed that the steady-state is completely analogous to a stationary-state. As such we can employ all the methods of dealing with the latter in working with periodic hamiltonians, keeping in mind though that the space we are working in is the extended space $(\mathbf{R} + \mathbf{T})$ with the inner product given by Eq.(4). In the following we discuss two of these techniques, viz., the variational method and perturbation theory, in detail as these are important for the work to be presented later in the paper.

A. Variational method

Since $\Phi(\mathbf{r}, t)$ satisfies Eq.(1), it is easy to show that the functional $E[\Phi]$ defined by Eq.(2) is stationary with respect to variations in Φ at the solution point if Φ is normalised in the $(\mathbf{R} + \mathbf{T})$ space. This then provides a method of obtaining approximate solutions of the Eq. (1) by making

$$\delta E[\Phi] = 0 \quad \dots(5)$$

subject to the constraint that

$$\{\langle \Phi | \Phi \rangle\} = 1 \quad \dots(6)$$

with E as the Lagrange multiplier. In reality the function Φ satisfies a stronger condition because it represents the solution of the Schrodinger equation. Since the norm $\langle \psi | \psi \rangle$ of a wavefunction ψ does not change with time

due to the hermiticity of the hamiltonian in $\mathbf{R}$, the constraint above is always satisfied once the wavefunction is normalised in $\mathbf{R}$ space. On the other hand, because Eq.(1) is obtained under the constraint of Eq. (6), all its solutions do not have a time-independent norm in $\mathbf{R}$ although their time averaged norm $\{\langle \Phi | \Phi \rangle\}$ in $\mathbf{R} + \mathbf{T}$ has been fixed to be 1. Out of all possible solutions, only those functions $\chi(\mathbf{r}, t)$ which remain properly normalised at all times, i.e., their norm $\langle \chi | \chi \rangle$ in $\mathbf{R}$ does not change with time, are physically meaningful. Proper normalisation of the wavefunction at all times can be ensured if $E[\chi]$ is made stationary subject to the condition that $\langle \chi | \chi \rangle = 1$. This results in the equation

$$[H - i(\partial/\partial t)] \chi(\mathbf{r}, t) = E(t) \chi(\mathbf{r}, t) \quad \dots(7)$$

with a time-dependent Lagrange multiplier $E(t)$. Equation (7) is an alternate representation of the time-dependent Schrodinger equation with the total wavefunction being¹⁰ $\Psi(\mathbf{r}, t) = \chi(\mathbf{r}, t) \exp(-i \int_0^t E(t') dt')$. Since $\Phi(\mathbf{r}, t)$ and $\chi(\mathbf{r}, t)$ describe the same wavefunction, they are both periodic and are related as¹¹

$$\Phi(\mathbf{r}, t) = \chi(\mathbf{r}, t) e^{-i\theta(t)} \quad \dots(8)$$

where $\theta(t)$ is a real periodic function of time such that

$$d\theta/dt = E(t) - E \quad \dots(9)$$

Because $\theta(t)$ is periodic in time, the quasi-energy E is the time-average of $E(t)$ as is evident from the equation above. In terms of χ , the quasi-energy is obtained from Eq. (2) with Φ replaced by χ . For perturbative calculations it is much more convenient^{10,11} to work in terms of χ rather than Φ , as will be discussed in the following section. We will also use the variational property of the quasi-energy with respect to χ to develop¹³ a variation-perturbation method for time-dependent perturbations.

B. Perturbation theory

As mentioned above, in addition to the ease of keeping the time-dependent wavefunction normalised, it is also better to do perturbation theory in terms of the transformed wavefunction χ . This is because χ is obtained by separating out¹⁰ the overall phase factor $\theta(t)$ from the full wavefunction. One therefore does not have to worry about its contribution — which is very difficult to keep track of at all orders — in the perturbative expansion of the wavefunction. Notice that the expectation value of any operator is not affected by removing this factor out

of the wavefunction. This is similar to stationary-state perturbation theory where the phase part involving the energy of the state is factored out right in the beginning

Now consider a system with the unperturbed hamiltonian $H^{(0)}$, which is time-independent and the corresponding wavefunction and energy $\Phi^{(0)}$ and $E^{(0)}$, respectively. When the system is subjected to a time-dependent perturbation $H^1(\mathbf{r}, t)$, its steady-state transformed wavefunction is given by $\chi(\mathbf{r}, t)$ which satisfies the conditions¹⁰

$$\langle \chi | \chi \rangle = 1 \quad \dots(10)$$

and

$$\langle \chi^{(0)} | \chi \rangle = \langle \chi | \chi^{(0)} \rangle \quad \dots(11)$$

where $\chi^{(0)} = \Phi^{(0)}$, at all times. The second condition arises from the fact that the overall phase¹⁰ that has been taken out is the factor multiplying $\chi^{(0)}$ if the full time-dependent wavefunction is expanded in terms of the wavefunctions of the unperturbed hamiltonian. As such its phase is fixed once and for all and no arbitrary imaginary multiple of the zeroth-order wavefunction can be added to the perturbed wavefunctions of various orders. At the solution point the eigenvalue $E(t)$ is given, as is easily seen from Eq.(7), by the expression

$$E(t) = E^{(0)} + \text{Re} \frac{\langle \chi^{(0)} | H^1 | \chi \rangle}{\langle \chi^{(0)} | \chi \rangle} \quad \dots(12)$$

and the quasi-energy

$$E = (1/T) \int_0^T E(t) dt \quad \dots(13)$$

In the perturbative regime, both χ and $E(t)$ are expanded as

$$\chi(\mathbf{r}, t) = \sum_{i=0}^{\infty} \chi^{(i)}(\mathbf{r}, t) \quad \dots(14)$$

$$E = \sum_{i=0}^{\infty} E^{(i)} \quad \dots(14)$$

where $\chi^{(i)}$ satisfy

$$\{H^{(0)} - E^{(0)} - i(\partial/\partial t)\} \chi^{(i)} + \{H^1(\mathbf{r}, t) - E^{(i)}\} \chi^{(i-1)} = 0 \quad \dots(15)$$

and

$$\{H^{(0)} - E^{(0)} - i(\partial/\partial t)\} \chi^{(0)} = 0$$

$$- \sum_{j=2}^i E^{(j)} \chi^{(i-j)}(\mathbf{r}, t) = 0 \text{ for } i \neq 1 \quad \dots(16)$$

Due to its variational nature, the average energy obeys the $2n+1$ rule and its variational corollary. Accordingly, wavefunction correct only up to order n is required to obtain energy up to order $2n+1$. Further, the even-order energy change $E^{(2n)}$ is stationary with respect to $\chi^{(n)}$, if χ is known correctly to order $n-1$. This leads to the equation for $\chi^{(n)}$. Thus, employing the variational expression [Eq.(2) divided by the norm $\langle \chi | \chi \rangle$] for the quasi-energy and using the wavefunction expanded only up to the first order, we obtain the following expressions for energy corrections up to the second order:

$$E^{(1)} = \langle \chi^{(0)} | H^1(\mathbf{r}, t) | \chi^{(0)} \rangle$$

$$E^{(2)} = \langle \chi^{(1)} | H^{(0)} - E^{(0)} - i(\partial/\partial t) | \chi^{(0)} \rangle + \langle \chi^{(0)} | H^1 | \chi^{(1)} \rangle \quad \dots(17)$$

Notice that making $E^{(2)}$ stationary with respect to variations in $\chi^{(1)}$ gives the correct equation for it. Now expanding the wavefunction up to the second order, and making use of the equation for $\chi^{(1)}$ derived from $E^{(2)}$ above, we get

$$E^{(3)} = \langle \chi^{(1)} | H^1 | \chi^{(1)} \rangle$$

$$E^{(4)} = \langle \chi^{(2)} | \{H^{(0)} - E^{(0)} - i(\partial/\partial t)\} | \chi^{(0)} \rangle + \langle \chi^{(2)} | H^1 - E^{(1)}(t) | \chi^{(1)} \rangle \quad \dots(18)$$

It is easily seen that one obtains the correct equation of motion for $\chi^{(2)}$ if the first-order change in $E^{(4)}$ is made to vanish with respect to variations in $\chi^{(2)}$. In deriving the energy expressions above, the wavefunction is assumed to be normalized up to the appropriate order (to the first order for $E^{(1)} \dots E^{(3)}$ and to the second order for $E^{(4)}$). Thus stationary nature of the even-order quasi-energies offers a variational method for obtaining the corrections to the unperturbed wavefunction. We will be making use of it in performing our calculations below. With this we complete our discussion of perturbation theory and its variational formulation in the steady state formalism for periodic time dependent hamiltonians. In the discussion above, we have worked in terms of the wavefunction. We will see below that the results derived

above are completely general and are also applicable when a many-electron system is described within the Kohn-Sham¹⁷ formulation of time-dependent density-functional theory which we now discuss.

II. Time-dependent density-functional theory

After the development of stationary-state DFT^{4,5}, and because it provided a convenient method of dealing with many-electron systems, efforts were made to develop its time-dependent counterpart. Like the stationary-state theory, the basic variable in time-dependent density functional theory (TDDFT) is the time-dependent (TD) density $\rho(\mathbf{r}, t)$ which contains all the information about the system. However, it was nearly two decades after the development of the stationary-state DFT that TDDFT came into being. Seminal work in the development of TDDFT was done by Deb and Ghosh¹⁸ and by Bartolotti^{19,20} who proved the Hohenberg-Kohn²¹ theorem for hamiltonians periodic in time. Since a system with time-dependent density also has currents, TDDFT has a close connection with the hydrodynamic formulation²² of quantum-mechanics. This connection was established in the work of Deb and Ghosh¹⁸ as well as in that of Bartolotti^{19,20}. However, a general theorem establishing a map between the TD potential and density was proved later by Runge and Gross²³. It states that if all time-dependent systems evolved from the same initial wavefunction ψ_0 then the TD potential $v(\mathbf{r}, t)$, and therefore the hamiltonian $H(\mathbf{r}, t)$ and the wavefunction $\psi(\mathbf{r}, t)$ are all unique functionals of the density $\rho(\mathbf{r}, t)$. It should be noted though that the potential can be determined only up to a purely time-dependent function $C(t)$ and the wavefunction up to a phase determined by $C(t)$. The only condition that the potential has to satisfy for the proof is that it be expandable in a Taylor series in time around the initial time t_0 . Further, the density can be determined by making the action integral

$$A[\rho(\mathbf{r}, t)] = \int_{t_0}^{\infty} dt \langle \psi | H - i(\partial/\partial t) | \psi \rangle \quad \dots(19)$$

stationary with respect to variations in $\rho(\mathbf{r}, t)$. The upper limit in the time integral has been taken to be ∞ because $v(\mathbf{r}, t)$ and therefore $\psi(\mathbf{r}, t)$ is a functional of the density $\rho(\mathbf{r}, t')$ for t' ranging²⁴ from t_0 and ∞ .

As discussed above, TDDFT is similar to the hydrodynamic formulation of quantum-mechanics Runge and Gross also derive²³ the hydrodynamic equations that the density and the current follow. Accordingly, the density

$$\rho(\mathbf{r}, t) = \int |\psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N, t)|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N \quad \dots(20)$$

and the current density

$$\mathbf{j}(\mathbf{r}, t) = (1/2i) \int \{ \psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N, t) \nabla \psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N, t) - \psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N, t) \nabla \psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N, t) \} d\mathbf{r}_2 \dots d\mathbf{r}_N \quad \dots(21)$$

satisfy

$$[\partial \rho(\mathbf{r}, t) / \partial t] + \nabla \cdot \mathbf{j}(\mathbf{r}, t) = 0 \quad \dots(22)$$

which is the continuity equation and

$$[\partial \mathbf{j}(\mathbf{r}, t) / \partial t] = \mathbf{P}[\rho](\mathbf{r}, t) \quad \dots(23)$$

which is the momentum-balance equation. The three component functional $\mathbf{P}$ is the sum²⁵ of various forces that influence the motion of the electrons. These equations are to be solved with the initial condition specified by $\psi_0(\mathbf{r}, t)$.

The stationarity of the action integral is also used to derive the time-dependent Kohn-Sham (TDKS) equation. To obtain the TDKS equation, we first identify the universal component of the action integral defined above. It is obtained by subtracting from the action integral the energy due to the external potential. Thus the universal functional

$$B[\rho] = A[\rho] - \int_{t_0}^{\infty} dt \int v(\mathbf{r}, t) \rho(\mathbf{r}, t) d\mathbf{r} \quad \dots(24)$$

The functional B comprises the kinetic energy and the electron-electron interaction energy. We also define another density functional - kinetic energy functional - similar to the kinetic energy for the time-independent case as

$$S[\rho(\mathbf{r}, t)] = \int_{t_0}^{\infty} dt \langle \psi | \nabla^2 | \psi \rangle \quad \dots(25)$$

Now we assume the density to be non-interacting v-representable so that it is given by the formula

$$\rho(\mathbf{r}, t) = \sum_j \Phi_j^*(\mathbf{r}, t) \Phi_j(\mathbf{r}, t) \quad \dots(26)$$

where Φ_j are the solutions of

$$\{ -(1/2) \nabla^2 + v_s(\mathbf{r}, t) \} \Phi_j(\mathbf{r}, t) = i(\partial/\partial t) \Phi_j(\mathbf{r}, t) \quad \dots(27)$$

The kinetic-energy functional corresponding to this non-interacting system is

$$S_0[\rho(\mathbf{r}, t)] = \int_{t_0}^{\infty} dt \sum_j \langle \Phi_j | - (1/2) \nabla^2 - i(\partial/\partial t) | \Phi_j \rangle \quad \dots(28)$$

and the action integral is given as

$$A[\rho] = S_0[\rho] + \int_{t_0}^{\infty} dt \int v_s(\mathbf{r}, t) \rho(\mathbf{r}, t) d\mathbf{r} \quad \dots(29)$$

Since the stationarity of the action integrals of both Eqs (19) and (20) give the same density, it is clear that

$$v_s(\mathbf{r}, t) = v(\mathbf{r}, t) + \int \frac{\rho}{|\mathbf{r} - \mathbf{r}'|} - \frac{\delta A_{xc}[\rho]}{\delta \rho(\mathbf{r}, t)} \quad \dots(30)$$

where, by construction the exchange-correlation component of the action is given as

$$A_{xc}[\rho] = B[\rho] - \int_{t_0}^{\infty} dt \left(\frac{1}{2} \int \int \frac{\rho(\mathbf{r}, t) \rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \right) + S[\rho] - S_0[\rho] \quad \dots(31)$$

With this, the derivation of the TDKS equation is complete. The density for a time dependent Hamiltonian can be obtained by solving an equivalent non-interacting problem with the effective potential given by Eq.(30) self-consistently. We now specialise to the case of periodic time-dependent hamiltonians which are central to describing the optical response properties of atoms and molecules.

Hamiltonians periodic in time

The general discussion above applies equally well to the particular case of applied time-dependent potentials which are periodic in time. Such potentials arise in describing the interaction of optical fields with an electronic system. For such potentials it is easily seen by substituting the wavefunctional form $\Psi(\mathbf{r}, t) = \chi(\mathbf{r}, t) e^{-i \int_{t_0}^t E(t') dt'}$ in the expression(Eq.19) for action integral that it is given as

$$A[\rho] = \int_0^T \langle \chi | \left(H - i \frac{\partial}{\partial t} \right) | \chi \rangle dt - \int_0^T E(t) \langle \chi | \chi \rangle dt \quad \dots(32)$$

where $E(t)$ is given by the solution of Eq.(7). As such the action principle for periodic hamiltonians is equivalent to making the functional of Eq.(2) stationary with $E(t)$ playing the role of the Lagrange multiplier to ensure that χ is normal in the R space at all times. For such hamiltonians one can therefore work in terms of the quasi-energy functional. As was discussed earlier, this has the advantage that quasi-energy has a direct physical interpretation. Thus the response properties can also be related to the changes in the quasi-energy. For these reasons, we also work in terms of the quasi-energy. Notice that it too is a functional of the time-dependent density

and becomes stationary for the exact density. As such in this section we cast the time-dependent Kohn-Sham equation in the language of steady-state formalism of Sambe and then develop perturbation theory within this approach in the next section.

To derive¹³ KS equations in the steady-state formalism, consider a system of non-interacting Fermions in a potential $v_s(t)$ periodic in time with period T which gives the same density as the interacting system, so that

$$\rho(\mathbf{r}, t) = \sum_j |u_j(\mathbf{r}, t)|^2, \quad \dots(33)$$

where $u_j(\mathbf{r}, t)$ satisfy

$$\left[-\frac{1}{2} \nabla^2 + v_s(\mathbf{r}, t) - i \frac{\partial}{\partial t} \right] u_j(\mathbf{r}, t) = 0 \quad \dots(34)$$

By construction $u_j(\mathbf{r}, t)$ are the time-dependent KS orbitals. Since $v_s(t)$ is periodic, $u_j(\mathbf{r}, t) = \phi_j(\mathbf{r}, t) e^{-i \epsilon_j t}$, where $\phi_j(\mathbf{r}, t)$ are also periodic (time-period T) and satisfy

$$\left[-\frac{1}{2} \nabla^2 + v_s(\mathbf{r}, t) - i \frac{\partial}{\partial t} \right] \phi_j(\mathbf{r}, t) = \epsilon_j \phi_j(\mathbf{r}, t) \quad \dots(35)$$

We refer to ϵ_j which are time-independent, as quasi Kohn-Sham eigenvalues. Note that the expression for the density in terms of $\phi_j(\mathbf{r}, t)$ or $u_j(\mathbf{r}, t)$ is the same. Now following the general arguments given in the previous section to arrive at Eq.(30) we get

$$v_s(\mathbf{r}, t) = v_{ext}(\mathbf{r}, t) + \frac{\delta \{E_H[\rho(\mathbf{r}, t)]\}}{\delta \rho(\mathbf{r}, t)} + \frac{\delta \{E_{xc}[\rho(\mathbf{r}, t)]\}}{\delta \rho(\mathbf{r}, t)} \quad \dots(36)$$

where $\{E_H\}$ and $\{E_{xc}\}$ are the time-averaged Hartree and exchange-correlation energies, respectively. The total energy in terms of the Kohn-Sham orbitals is given as

$$E[\rho] = \left\{ \sum_i \epsilon_i + E_{Hxc}[\rho] - \int \frac{\delta \{E_{Hxc}\}}{\delta \rho(\mathbf{r}, t)} \rho(\mathbf{r}, t) d\mathbf{r} \right\}_{average} \quad \dots(37)$$

where $\{E_{Hxc}\}$ represents the time-average of the sum of the Hartree, exchange and correlation energies. Observe the similarity between Eqs(36) and (37) and the corresponding quantities in the stationary-state Kohn-Sham¹⁷ theory.

As pointed out earlier, for convenience in applying perturbation theory and also to ensure that the orbitals

are normalised at all times, it is better to transform these equations by separating out the time-dependent phase $\theta_j(t)$ from each orbital $\phi_j(\mathbf{r}, t)$ and work in terms of the transformed orbitals $\chi_j(\mathbf{r}, t)$ instead. As a result of this, each KS eigenvalue becomes time-dependent with its time-average equal to the quasi KS eigenvalue. The relationship between the orbitals $\phi_j(\mathbf{r}, t)$ and $\chi_j(\mathbf{r}, t)$ and the phase $\theta_j(t)$ is given by Eq.(8) where $\theta_j(t)$ is determined by Eq. (9) with KS eigenvalues $\epsilon_j/\epsilon_j(t)$ in place of the energy $E/E(t)$. We now describe perturbation theory in terms of these transformed orbitals

III. Perturbation theory in time-dependent Kohn-Sham formalism

To develop perturbation theory we now consider $v_{\text{ext}}(\mathbf{r}, t)$ to be made up two parts:

$$v_{\text{ext}}(\mathbf{r}, t) = v_0(\mathbf{r}) + v^{(1)}(\mathbf{r}, t) \quad \dots(38)$$

where $v_0(\mathbf{r})$ is a time-independent potential which is the part of the unperturbed hamiltonian, and,

$$v^{(1)}(\mathbf{r}, t) = (1/2)v^{(1)}(\mathbf{r})(e^{i\omega t} + e^{-i\omega t}) \quad \dots(39)$$

is the applied perturbation. The Hamiltonian is accordingly

$$H = H^{(0)} + H'(\mathbf{r}, t) \quad \dots(40)$$

where $H'(\mathbf{r}, t)$ is the sum of $v^{(1)}(\mathbf{r}, t)$ and corrections to the Hartree and the exchange-correlation potentials arising from the self-consistent change in the density due to the applied perturbation. Analogous to Eq.(7), the transformed Kohn-Sham equation is

$$[H^{(0)} + H' - i(\partial/\partial t)]\chi_j(\mathbf{r}, t) = \epsilon_j(t)\chi_j(\mathbf{r}, t) \quad \dots(41)$$

where

$$\epsilon_j(t) = \epsilon_j^{(0)} + \text{Re} \frac{\langle \chi_j^{(0)} | \sum_{n=1} H^{(n)}(t) | \chi_j \rangle}{\langle \chi_j^{(0)} | \chi_j \rangle} \quad \dots(42)$$

where the superscript '0' refers to the unperturbed state. The orbital quasi-energy ϵ_j is given as

$$\epsilon_j = \frac{1}{T} \int_0^T dt \epsilon_j(t) \quad \dots(43)$$

Each of the transformed orbital satisfies the normalisation condition

$$\langle \chi_i | \chi_j \rangle = \delta_{ij} \quad \dots(44)$$

and

$$\langle \chi_i | \chi_j^{(0)} \rangle = \langle \chi_j^{(0)} | \chi_i \rangle \quad \dots(45)$$

Notice that the expressions for the density and the total energy in terms of transformed orbitals remain the same as given above by Eq. (37), although ϵ_j in Eq.(35) are now replaced by their time-dependent counterpart as given by Eq. (42). The perturbation expansion for the orbitals, the density, the perturbed Hamiltonian H' and ϵ_j is

$$\begin{aligned} \chi(\mathbf{r}, t) &= \sum_{k=0}^{\infty} \chi^{(k)}(\mathbf{r}, t); \\ \rho(\mathbf{r}, t) &= \sum_{k=0}^{\infty} \rho^{(k)}(\mathbf{r}, t); \\ H'(\mathbf{r}, t) &= \sum_{k=1}^{\infty} H^{(k)}(\mathbf{r}, t); \\ \epsilon_j(t) &= \sum_{k=0}^{\infty} \epsilon_j^{(k)}(t) \end{aligned} \quad \dots(46)$$

and the equation for $\chi^{(n)}$ is

$$\left[H^{(0)} - \epsilon_j^{(0)} - i \frac{\partial}{\partial t} \right] \chi_j^{(n)} + \sum_{k=1}^n (H^{(k)} - \epsilon_j^{(k)}) \chi_j^{(n-k)} = 0 \quad \dots(47)$$

where by Eqs (44) and (45)

$$\langle \chi_j^{(0)} | \chi_j^{(n)} \rangle = -\frac{1}{2} \sum_{k=1}^{n-1} \langle \chi_j^{(k)} | \chi_j^{(n-k)} \rangle \quad \dots(48)$$

Substituting the transformed orbitals in the expression for the energy Eq. (37) and properly rearranging^{26,27} the terms obtained, we get

$$\begin{aligned} E^{(1)} &= \left\{ \int v^{(1)}(\mathbf{r}, t) \rho^{(0)}(\mathbf{r}) d\mathbf{r} \right\}_{\text{average}} \\ E^{(2)} &= \left\{ \sum_i \left[\langle \chi_i^{(1)} | \mathcal{H}_0 - \epsilon_i^{(0)} | \chi_i^{(1)} \rangle + \langle \chi_i^{(1)} | v^{(1)} | \chi_i^{(0)} \rangle + \langle \chi_i^{(0)} | v^{(1)} | \chi_i^{(1)} \rangle \right] + \right. \\ &\quad \left. + \frac{1}{2} \int \frac{\delta^2 E_{Hxc}[\rho]}{\delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2)} \rho^{(1)}(\mathbf{r}_1, t) \rho^{(1)}(\mathbf{r}_2, t) d\mathbf{r}_1 d\mathbf{r}_2 \right\}_{\text{average}} \\ E^{(3)} &= \left\{ \sum_i \langle \chi_i^{(1)} | H^{(1)} - \epsilon_i^{(1)} | \chi_i^{(1)} \rangle + \right. \\ &\quad \left. + \frac{1}{6} \int \frac{\delta^3 E_{Hxc}[\rho]}{\delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2) \delta \rho(\mathbf{r}_3)} \rho^{(1)}(\mathbf{r}_1, t) \rho^{(1)}(\mathbf{r}_2, t) \rho^{(1)}(\mathbf{r}_3, t) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \right\}_{\text{average}} \end{aligned}$$

$$\begin{aligned}
E^{(4)} = & \left\{ \sum_i \langle \chi_i^{(2)} | \mathcal{H}_0 - \epsilon_i^{(2)} | \chi_i^{(2)} \rangle + \langle \chi_i^{(2)} | \tilde{H}^{(1)} - \epsilon_i^{(1)} | \chi_i^{(1)} \rangle + \langle \chi_i^{(1)} | \tilde{H}^{(2)} - \epsilon_i^{(1)} | \chi_i^{(2)} \rangle \right. \\
& + \frac{1}{2} \int \frac{\delta^2 E_{Hxc}[\rho]}{\delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2)} \rho^{(2)}(\mathbf{r}_1, t) \rho^{(2)}(\mathbf{r}_2, t) d\mathbf{r}_1 d\mathbf{r}_2 \\
& + \frac{1}{2} \int \frac{\delta^3 E_{Hxc}[\rho]}{\delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2) \delta \rho(\mathbf{r}_3)} \rho^{(1)}(\mathbf{r}_1, t) \rho^{(1)}(\mathbf{r}_2, t) \rho^{(2)}(\mathbf{r}_3, t) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \\
& \left. + \frac{1}{24} \int \frac{\delta^4 E_{Hxc}[\rho]}{\delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2) \delta \rho(\mathbf{r}_3) \delta \rho(\mathbf{r}_4)} \rho^{(1)}(\mathbf{r}_1, t) \rho^{(1)}(\mathbf{r}_2, t) \right. \\
& \left. \times \rho^{(1)}(\mathbf{r}_3, t) \rho^{(1)}(\mathbf{r}_4, t) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \right\}_{\text{average}} \quad \dots(49)
\end{aligned}$$

where

$$\mathcal{H}_0 = H^{(0)} - i \frac{\partial}{\partial t} \quad \dots(50)$$

As is clear from these expressions, only $\chi_i^{(1)}$ is required to obtain energy up to order 3. Also due to variational nature of the energy functional, the even-order energies, $E^{(2)}$ and $E^{(4)}$, are stationary with respect to $\chi_i^{(1)}$ and $\chi_i^{(2)}$ respectively. This is evident from the fact that stationarity of $E^{(2)}$ and $E^{(4)}$ leads to the correct equations for these orbitals.

Alternatively, the stationary nature of the even-order energies can also be used to obtain the induced orbitals and energies variationally, as we do in this paper. The expression for $H^{(1)}$ is

$$H^{(1)}(\mathbf{r}, t) = v^{(1)}(\mathbf{r}, t) + \int \frac{\delta^2 E_{Hxc}}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}_1)} \rho^{(1)}(\mathbf{r}_1, t) d\mathbf{r}_1 \quad \dots(51)$$

Similar expressions for the higher-order corrections to the Hamiltonian can be derived and involve higher-order derivatives of the Hartree and exchange-correlation energy functionals. The procedure adopted above is quite general and can be employed to calculate energy changes to any desired order. Furthermore, if the orbitals are known correctly to order $(n-1)$, the even-order energies $E^{(2n)}$ are stationary with respect to $\chi^{(n)}$; leading variationally to the perturbative equation for the n th order correction to the orbitals. This completes the formal development of variation-perturbation theory for periodic time-dependent potentials. We now apply it to calculate linear and nonlinear optical response properties of the noble gas atoms helium, neon and argon and show by comparing the well investigated results of these atoms that accurate numbers for these properties are obtained with density-functional theory. In these applications we restrict ourselves to below the first transition frequency where the stationary point of the quasi-energy is a minimum.

IV. Optical response properties of noble gas atoms

Using the stationary nature of the quasi-energy, in this section we perform variational calculations of the fre-

quency-dependent linear and nonlinear response properties of helium, neon and argon. We work within the dipole approximation and calculate the linear polarizabilities $\alpha(\omega)$ and nonlinear polarizabilities $\gamma(\omega; \omega, -\omega, \omega)$ which corresponds to degenerate four wave mixing (DFWM) and $\gamma(3\omega; \omega, \omega, \omega)$ responsible for third harmonic generation (THG). Linear polarizability $\alpha(\omega)$ and the DFWM coefficient $\gamma(\omega; \omega, -\omega, \omega)$ are directly related to the second- and fourth-order energy changes given above as

$$\alpha(\omega) = -4E^{(2)} \quad \dots(52)$$

and

$$\gamma(\omega; \omega, -\omega, \omega) = -64E^{(4)} \quad \dots(53)$$

On the other hand, THG coefficient is not directly related to $E^{(4)}$. It is instead given^{14,27} as

$$\begin{aligned}
\gamma(3\omega; \omega, \omega, \omega) = & 96 \left(\sum_i \langle \chi_i^{(1)}(+3) | \tilde{H}^{(2)}(+2) - \epsilon_i^{(2)}(+2) | \chi_i^{(1)}(+1) \rangle \right. \\
& + \langle \chi_i^{(1)}(-1) | \tilde{H}^{(2)}(+2) - \epsilon_i^{(2)}(+2) | \chi_i^{(1)}(-3) \rangle \\
& + \langle \chi_i^{(1)}(+3) | \tilde{H}^{(1)}(+1) - \epsilon_i^{(1)}(+1) | \chi_i^{(2)}(+2) \rangle \\
& + \langle \chi_i^{(2)}(-2) | \tilde{H}^{(1)}(+1) - \epsilon_i^{(1)}(+1) | \chi_i^{(1)}(-3) \rangle \\
& + \langle \chi_i^{(1)}(-1) | \tilde{H}^{(1)}(-3) - \epsilon_i^{(1)}(-3) | \chi_i^{(2)}(+2) \rangle \\
& \left. + \langle \chi_i^{(2)}(-2) | \tilde{H}^{(1)}(-3) - \epsilon_i^{(1)}(-3) | \chi_i^{(1)}(+1) \rangle \right) \\
& + \int \frac{\delta^3 E_{Hxc}}{\delta \rho(\mathbf{r}, t) \delta \rho(\mathbf{r}', t) \delta \rho(\mathbf{r}'', t)} \rho_{+1}^{(1)}(\mathbf{r}, t) \rho_{-3}^{(1)}(\mathbf{r}', t) \rho_{+2}^{(2)}(\mathbf{r}'', t) d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' \\
& + \frac{1}{3!} \int \frac{\delta^4 E_{Hxc}}{\delta \rho(\mathbf{r}, t) \delta \rho(\mathbf{r}', t) \delta \rho(\mathbf{r}'', t) \delta \rho(\mathbf{r}''', t)} \\
& \times \rho_{+1}^{(1)}(\mathbf{r}, t) \rho_{+1}^{(1)}(\mathbf{r}', t) \rho_{+1}^{(1)}(\mathbf{r}'', t) \rho_{-3}^{(1)}(\mathbf{r}''', t) d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}''' \quad \dots(54)
\end{aligned}$$

where the argument of each orbital χ indicates the frequency at which it is being calculated [see Eqs (63) and (64) below]. The equation above means that the calculation of THG coefficient requires the first-order orbitals at two frequencies, ω and 3ω . Thus to calculate $\gamma(3\omega; \omega, \omega, \omega)$ we first obtain the first- and second-order orbital by applying the perturbation at frequency ω . We then perform another calculation by considering the applied field of frequency 3ω which gives the first-order orbital at this frequency. Substituting these in Eq.(54) gives the THG coefficient.

We do our calculations with two sets of unperturbed orbitals which are obtained with different approxima-

tions for the exchange-correlation energy functional. First, we treat the exchange-correlation effects within the local-density approximation (LDA). As is well known, the asymptotic effective potential, and therefore the orbitals in that region, are not obtained correctly in the LDA. Since the LDA orbitals are less tightly bound than the exact ones, they lead to polarizabilities and hyperpolarizabilities which are overestimates of their exact counterparts. The error is roughly 10% for the linear and nearly 100% for the nonlinear polarizabilities. It is clear that proper behaviour of orbitals in the asymptotic region, which in turn depends on the potential there, is quite crucial to obtaining accurate estimates of these quantities. In order to correct the asymptotic nature of the potential, van Leeuwen and Baerends (LB) have proposed a correction to the LDA potential that improves the quality of the orbitals substantially in comparison to the LDA orbitals. Our second set of calculations is performed using the orbitals generated by this potential. As discussed below, the results of these calculations are highly accurate for both the linear as well as the nonlinear polarizabilities of the atoms considered. This then shows that by applying DFT highly accurate estimates of these properties can be made with relatively less computational effort. In the following we first discuss the exchange-correlation functionals used in obtaining the unperturbed orbitals and in performing the perturbative calculations. We then discuss the variational form chosen for the orbitals and finally present our results.

A. Exchange-correlation functionals

As mentioned above, we have performed our calculations by employing the unperturbed orbitals obtained from the LDA as well as from the LB approximation for the exchange-correlation energy. For perturbation calculations, on the other hand, we use the adiabatic local density approximation (ALDA). In the following, we describe these functionals briefly.

1. Local density approximation

In the local density approximation^{4,5} the exchange-correlation energy is obtained by calculating the energy density at each point in space by the expression for the homogeneous electron gas. Thus the exchange energy²⁹

$$E_x^{LDA}[\rho] = d_0 \int \rho^{4/3}(\mathbf{r}) d\mathbf{r} \quad \dots(55)$$

with $d_0 = -(3/4) (3/\pi)^{1/3}$. For the correlation energy we use the Gunnarsson-Lundquist³⁰ parametrization so that

$$E_c^{LDA}[\rho] = c \int \rho(\mathbf{r}) \left[(1+x^3) \ln \left(1 + \frac{1}{x} \right) + \frac{x}{2} - x^2 - \frac{1}{3} \right] d\mathbf{r} \quad \dots(56)$$

with $c = -0.0333$, $x = r_s/A$, $A = 11.4$, where $r_s = [3/4\pi\rho(\mathbf{r})]^{1/3}$ is the local r_s value. The corresponding exchange and correlation potentials are calculated as the functional derivative of these functionals and are given as

$$v_x^{LDA}(\mathbf{r}) = - \left(\frac{3\rho(\mathbf{r})}{\pi} \right)^{1/3} \quad \dots(57)$$

and

$$v_c^{LDA}(\mathbf{r}) = c \ln \left(1 + \frac{1}{x} \right) \quad \dots(58)$$

2. van Leeuwen-Baerends potential

The behaviour of the LDA potential in the asymptotic regions is exponential rather than the correct³¹ $-1/r$. Because of this the LDA calculations give the outer electrons to be loosely bound. This is reflected in the highest occupied orbital eigenvalues obtained in the LDA calculations; whereas the correct value for it is³¹⁻³³ equal to minus the ionisation energy, the LDA gives a value of only half as much. If the LDA functional is improved³⁴⁻³⁶ by including gradient corrections to it, the energy values also improve but the tail region of the potential does not. To rectify this situation, van Leeuwen and Baerends²⁸ proposed a correction to be added directly to the potential so that its asymptotic structure becomes exact. Motivated by the accuracy of Becke's functional³⁶ for the exchange energy, the correction they add to the LDA potential is given as

$$v^{LB}(\mathbf{r}) = -\beta \rho^{1/3}(\mathbf{r}) \frac{1}{1 + 3\beta x \sinh^{-1}(x)} \quad \dots(59)$$

with $x = |\nabla \rho|/\rho^{4/3}$. Thus the total potential is given by

$$v_{xc}(\mathbf{r}) = v_{xc}^{LDA}(\mathbf{r}) + v^{LB}(\mathbf{r}) \quad \dots(60)$$

The parameter β is fixed by fitting the resulting potential in such a way that it resembles as closely as possible with the exact potential for the Be atom. The potential constructed in this manner leads³⁷ to accurate total en-

ergies and highest occupied orbital eigenvalues. This implies that the orbitals and the total density obtained by solving the KS equation with this potential are quite accurate. We have also used these orbitals to obtain response properties of the atoms considered in this paper.

3. Adiabatic local density approximation

The exchange-correlation energy functional for the time-dependent case is nonlocal in space as well as in time. However, like the static case, an excellent approximation is provided by considering the functional dependence to be local in both space and time. Thus the value of the functional is given by the same expression as the LDA except that the density input in this case becomes time-dependent. This is known as the adiabatic local density approximation (ALDA)⁸ and has been shown³⁸ to be a major component of the exact functional. In addition, all the higher order functional derivatives required for response properties calculations exist for this functional and they can also be easily calculated. Keeping all these points in mind, it is this functional that we use for the calculation of the perturbative changes in the exchange-correlation energy. It has already been demonstrated^{14,39} that ALDA, when employed in conjunction with accurate ground-state densities, leads to highly accurate results for the optical response properties. This is also borne out of the results presented below.

B. Variational form for the orbitals

The atoms that we consider in this paper are closed-shell systems and have only *s*- and *p*-type orbitals. The variational forms chosen²⁷ for the first-order change in these orbitals are

$$\chi_{ns}^{(1)}(\mathbf{r}, t) = \sqrt{\frac{1}{3}} f_{ns1}^{(1)}(\mathbf{r}, t) Y_{10}(\theta, \phi) \quad \dots(61)$$

and

$$\begin{aligned} \chi_{np0}^{(1)}(\mathbf{r}, t) &= \sqrt{\frac{4}{15}} f_{np2}^{(1)}(\mathbf{r}, t) Y_{20}(\theta, \phi) + \sqrt{\frac{1}{3}} f_{np0}^{(1)}(\mathbf{r}, t) Y_{00}(\theta, \phi) \\ \chi_{np1}^{(1)}(\mathbf{r}, t) &= \sqrt{\frac{1}{5}} f_{np2}^{(1)}(\mathbf{r}, t) Y_{2+1}(\theta, \phi) \\ \chi_{np-1}^{(1)}(\mathbf{r}, t) &= \sqrt{\frac{1}{5}} f_{np2}^{(1)}(\mathbf{r}, t) Y_{2-1}(\theta, \phi). \end{aligned} \quad \dots(62)$$

respectively. The subscript *n* indicates the orbital index and $Y_{lm}(\theta, \phi)$ represents the spherical harmonic function characterizing the angular part of induced orbitals.

Now we write down the variational forms for the second-order orbitals:

$$\chi_{ns}^{(2)}(\mathbf{r}, t) = \sqrt{\frac{4}{45}} f_{ns2}^{(2)}(\mathbf{r}, t) Y_{20}(\theta, \phi) + \sqrt{\frac{1}{9}} f_{ns0}^{(2)}(\mathbf{r}, t) Y_{00}(\theta, \phi) \quad \dots(63)$$

for the *s*-type and

$$\begin{aligned} \chi_{np0}^{(2)}(\mathbf{r}, t) &= \frac{9}{15} f_{np1}^{(2)}(\mathbf{r}, t) Y_{10}(\theta, \phi) + \sqrt{\frac{12}{175}} f_{np3}^{(2)}(\mathbf{r}, t) Y_{30}(\theta, \phi) \\ \chi_{np1}^{(2)}(\mathbf{r}, t) &= \sqrt{\frac{1}{25}} f_{np1}^{(2)}(\mathbf{r}, t) Y_{1+1}(\theta, \phi) + \sqrt{\frac{8}{175}} f_{np3}^{(2)}(\mathbf{r}, t) Y_{3+1}(\theta, \phi) \\ \chi_{np-1}^{(2)}(\mathbf{r}, t) &= \sqrt{\frac{1}{25}} f_{np1}^{(2)}(\mathbf{r}, t) Y_{1-1}(\theta, \phi) + \sqrt{\frac{8}{175}} f_{np3}^{(2)}(\mathbf{r}, t) Y_{3-1}(\theta, \phi) \end{aligned} \quad \dots(64)$$

for *p*-type orbitals. Each “*f*” function above has a form given by Eq.(67) below. For the applied potential of the form given by Eq.(39), the time-dependence of the “*f*” function to various orders is given as

$$f^{(1)}(\mathbf{r}, t) = f_+^{(1)}(\mathbf{r}) e^{i\omega t} + f_-^{(1)}(\mathbf{r}) e^{-i\omega t} \quad \dots(65)$$

and

$$f^{(2)}(\mathbf{r}, t) = f_+^{(2)}(\mathbf{r}) e^{2i\omega t} + f_-^{(2)}(\mathbf{r}) e^{-2i\omega t} + f_0^{(2)}(\mathbf{r}) \quad \dots(66)$$

The radial part of the induced orbitals above is represented by a superposition of Slater type orbitals (STO). A typical form of the radial function chosen is

$$f(r) = \sum_i C_i r^{n_i} e^{-\xi_i r} \quad \dots(67)$$

where n_i and ξ_i are the parameters of STO which are fixed and C_i are the linear variational parameters. The parameter $n_i \geq l_i + 1$, where l_i represents the spherical harmonics *f*(*r*) is multiplied by. The values of n_i and ξ_i are chosen in such a way so that $\chi_i^{(n)}(\mathbf{r})$ correctly represents the induced orbitals. We choose these parameters from the knowledge of HF ground-state orbitals⁴⁰ represented in terms of STOs. From these orbitals we obtain the expressions for the induced densities by using

$$\rho^{(1)}(\mathbf{r}, t) = \sum_i \left(\chi_i^{*(1)}(\mathbf{r}, t) \chi_i^{(0)}(\mathbf{r}) + \chi_i^{(1)}(\mathbf{r}, t) \chi_i^{*(0)}(\mathbf{r}) \right) \quad \dots(68)$$

and

$$\rho^{(2)}(\mathbf{r}, t) = \sum_i \left(\chi_i^{*(2)}(\mathbf{r}, t) \chi_i^{(0)}(\mathbf{r}) + \chi_i^{(2)}(\mathbf{r}, t) \chi_i^{*(0)}(\mathbf{r}) + \chi_i^{*(1)}(\mathbf{r}, t) \chi_i^{(1)}(\mathbf{r}, t) \right) \quad \dots(69)$$

along with Eqs (60-63). We point out that for closed-shell systems the first-order induced density $\rho^{(1)}(\mathbf{r}, t)$ has the same angular dependence as that of the applied

perturbation. This means that for our case the angular part of $\rho^{(1)}(\mathbf{r}, t)$ is completely specified by $\cos\theta$ ($Y_{10}(\theta, \phi)$), which is the angular component of the perturbing potential. This is a particular case of a theorem due to Eves and Epstein⁴¹ which states that for a system with all electrons in filled shells, the first-order induced density $\rho^{(1)}(\mathbf{r}, t)$ due to a perturbation of the form $v_M(\mathbf{r}) = E r P_M(\cos\theta)$ where $P_M(\cos\theta)$ is Legendre Polynomial of index M , has its angular dependence described entirely by $P_M(\cos\theta)$. The second-order induced density for spherical system is found²⁷ to be of the form

$$\rho^{(2)}(\mathbf{r}, t) = \rho_0^{(2)}(r, t)Y_{00}(\theta, \phi) + \rho_2^{(2)}(r, t)Y_{20}(\theta, \phi). \quad \dots(70)$$

Thus the second-order density has a constant plus one term with $\cos^2\theta$ angular dependence. In the following we discuss how the orbitals are kept orthonormal at all orders.

Ortho-normalization condition

As discussed in the beginning because of the hermiticity of the hamiltonian, the ortho-normalization conditions between the time-dependent perturbed orbitals at any time are the same as those between the unperturbed ones and have to be ensured at each order of the perturbative expansion. For this we take an approach employed by Hurst *et al*⁴² for the VP calculation of static response properties within the HF theory. To satisfy the ortho-normality condition (Eq. 48) we take the induced orbitals as

$$\begin{aligned} \chi_i^{(1)}(\mathbf{r}, t) &= f_i^{(1)}(\mathbf{r}, t) - \sum_{j=1}^N \langle \chi_j^{(0)} | f_i^{(1)} \rangle \chi_j^{(0)}(\mathbf{r}) \\ \chi_i^{(2)}(\mathbf{r}, t) &= f_i^{(2)}(\mathbf{r}, t) - \sum_{j=1}^N \left(\langle \chi_j^{(0)} | f_i^{(2)} \rangle + \langle \chi_i^{(1)} | \chi_j^{(1)} \rangle \right) \chi_j^{(0)}(\mathbf{r}) \end{aligned} \quad \dots(71)$$

where $f_i^{(1)}(\mathbf{r}, t)$ and $f_i^{(2)}(\mathbf{r}, t)$ are the unconstrained functions whose variational forms we represent by the linear combinations of STOs. With this we complete the discussion on the variational form for the induced orbitals and their ortho-normalization. Now we proceed on to present the results of our calculations.

C. Results and discussion

We now report the results of our calculations of response properties of helium, neon and argon by employing the approach outlined above. Presented in Table 1 are the static values $\alpha(0)$ of linear polarizabilities of these atoms, while their frequency dependence is displayed in Figs 1 - 3. These are compared with the *ab initio* results of Bishop and Lam⁴³ for He and with the

Table 1 – Static linear polarizabilities of helium, neon and argon atoms with LDA and LDA + LB orbitals in comparison with the *ab initio* and experimental numbers (in atomic units).

Atom	$\alpha(0)$			
	LDA	LDA + LB	<i>Ab initio</i>	Expt.
He	1.63	1.40	1.384 ⁴³	1.39
Ne	3.00	2.61	2.63 ⁴⁴	2.67
Ar	11.80	11.52	11.20 ⁴⁴	11.08

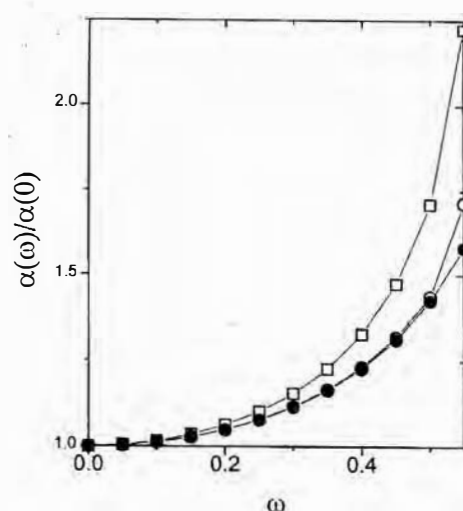


Fig. 1 – Plot of $\alpha(\omega)/\alpha(0)$ as a function of frequency ω for helium. The squares, open circles and filled circles represent the LDA, the LDA + LB and *ab initio* results⁴³, respectively.

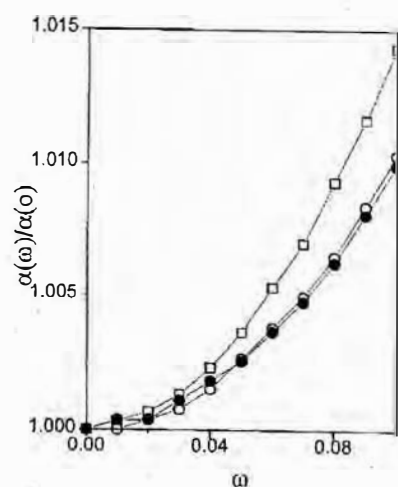


Fig. 2 – Plot of $\alpha(\omega)/\alpha(0)$ as a function of frequency ω for neon. The squares, open circles and filled circles represent the LDA, the LDA + LB and *ab initio* results⁴⁴ respectively.

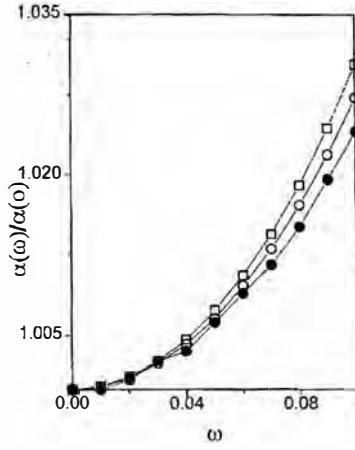


Fig. 3 – Plot of $\alpha(\omega)/\alpha(0)$ as a function of frequency ω for argon. The squares, open circles and filled circles represent the LDA, the LDA + LB and *ab initio* results⁴⁴, respectively.

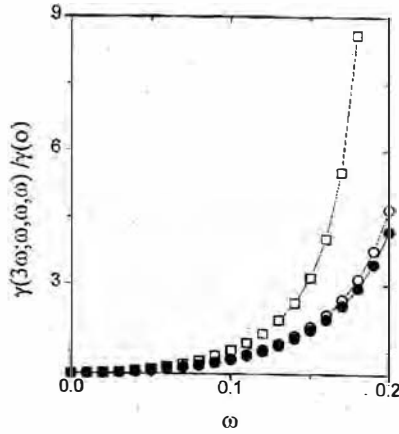


Fig. 4 – Plot of $\gamma(3\omega)/\gamma(0)$ (THG) as a function of frequency ω for helium. The squares, open circles and filled circles represent the LDA, the LDA + LB and *ab initio* results⁴⁶, respectively.

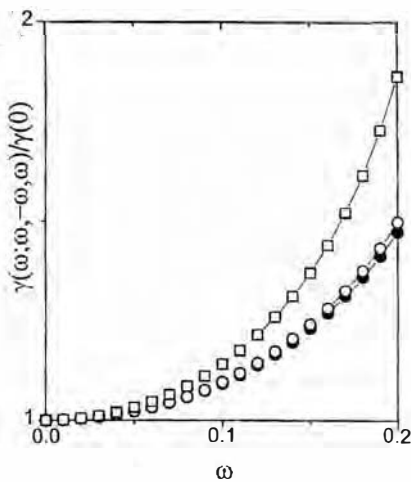


Fig. 5 – Plot of $\gamma(\omega)/\gamma(0)$ (DFWM) as a function of frequency ω for helium. The squares, open circles and filled circles represent the LDA, the LDA + LB and *ab initio* results⁴⁶, respectively.

MP2 results of Rice *et al.*⁴⁴ for Ne and Ar. As expected, the LDA ground-state orbitals overestimate the value of α at each frequency. Further, the LDA predicts it to be increasing faster than the *ab initio* calculation. However, when accurate orbitals obtained from the LB potentials are used, the match between the DFT results and those of *ab initio* calculations is excellent for the frequency range considered. We note that the optical range of frequencies extends up to about $\omega = 0.1$.

Next we present the results for the nonlinear polarizabilities of these atoms. Shown in Figs 4 and 5 is the dynamic behaviour of the DFWM and THG coefficients of helium with $\gamma^{\text{LDA}}(0) = 82.84$ a.u., $\gamma^{\text{LB}}(0) = 42.84$ a.u. and $\gamma^{\text{ab initio}}(0) = 43.10$ a.u. (Ref. 46). Like the linear polarizabilities, the nonlinear polarizabilities calculated with the LDA orbitals are larger than their *ab initio* counterparts. However, the error is much larger in this case. Further, both γ^{DFWM} and γ^{THG} obtained from the LDA orbitals increase much more rapidly with frequency as compared to the *ab initio* results. On the other hand, the LB orbitals lead to accurate results for both the magnitude and the frequency-dependence of these quantities.

Although accurate *ab initio* calculations of nonlinear polarizabilities over a range of frequencies have been performed for the helium atom, this is not the case for neon and argon. However, experimental numbers for

Table 2 – THG coefficients for helium, neon and argon atoms with and without the LB correction to the LDA along with their experimental values (in atomic units).

Atom	$\lambda = 6943 \text{ \AA}$			$\lambda = 10550 \text{ \AA}$		
	LDA	LDA+LB	Expt. ⁴⁸	LDA	LDA+LB	Expt. ⁴⁷
He	98.46	48.35	53.6 $\pm$ 7 53.6 $\pm$ 2.4	89.12	45.11	44.07 $\pm$ 4.8
Ne	230.30	103.68	119 $\pm$ 13 96.5 $\pm$ 4.8	202.67	95.50	78.27 $\pm$ 8.3
Ar	2532.8	1560.3	1691 $\pm$ 167 786 $\pm$ 48	1925	1275.1	1021.3 $\pm$ 107

Table 3 – DFWM coefficients for helium, neon and argon atoms with and without the LB correction to the LDA (in atomic units)

Atom	$\lambda = 6943 \text{ \AA}$		$\lambda = 10550 \text{ \AA}$	
	LDA	LDA+LB	LDA	LDA+LB
He	87.62	44.57	84.86	43.58
Ne	198.16	94.06	190.45	91.65
Ar	1863.0	1226.1	1725.5	1154.8

the THG coefficient are available for all three atoms at $\lambda = 6943 \text{ \AA}$ ($\omega = 0.0433 \text{ a.u.}$ and at $\lambda = 10550 \text{ \AA}$ ($\omega = 0.0658 \text{ a.u.}$). In Table 2 we compare the numbers obtained by us with the experimental values. It is evident that DFT calculations based on LB potential lead to highly accurate results for this coefficient whereas the LDA overestimates it by a large amount. In Table 3 we give the numbers for DFWM coefficients of these atoms at the wavelengths given above; there are no experimental numbers available for these coefficients. It is seen from the Table that LB orbitals give values which are much smaller than their LDA counterparts, and should also be close to experimental numbers. Notice that the THG coefficient is larger than the DFWM coefficient at all frequencies, as indeed is expected.

It is evident from the discussion above that the exchange-correlation functional that gives the asymptotic structure of the corresponding potential correctly, would lead to accurate results for the response properties. The LDA, on the other hand, overestimates these properties. The error is small for the linear case whereas for nonlinear properties it is quite large. Notice that in all these calculations, the changes in the energy are still calculated using ALDA. This then implies that ALDA is a reasonable approximation in the optical range of frequencies.

V. Concluding remarks

Time-dependent density-functional theory has come a long way since the first ad-hoc time-dependent calculation^{49,50} employing DFT methods was reported. Now it is being applied to calculate response properties of atoms and molecules^{13-15, 39,51} to describe^{7,8,12} the behaviour of atoms in intense laser fields and recently it has also been used to estimate^{52,53} the excited states of atoms. In this paper we have described the work done by us in the direction of developing and applying variation-perturbation method within this formalism. With the accuracy of the results obtained for atoms, it is clear that it can now be applied to obtain linear and nonlinear optical response properties of more complicated systems.

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