# TDDFT Microcredit Course TS66003 Assignment Submission by 16MT10035

Rochish Manda

B.Tech. 4$^{\text{th}}$ year, MME

IIT KHARAGPUR

June 14, 2020

## Part I

## Answer: 1

**KE of Non-interacting uniform electron gas (of density $\rho = \frac{N}{V}$) ...**

By symmetry, the Kohn-Sham potential $v_s(\mathbf{r})$ must be uniform or constant, and we take it to be zero. We impose boundary conditions within a cube of volume $\nu \longrightarrow \infty$, i.e., we require that the orbitals repeat from one face of the cube to its opposite face. The Kohn-Sham orbitals are then plane waves $\exp(i\mathbf{k} \cdot \mathbf{r}/\sqrt{\nu})$, with momenta or wavevectors $\mathbf{k}$ and energies $k^2/2$. The number of orbitals of both spins in a volume $\mathrm{d}^3k$ of wavevector space is $2[\nu/(2\pi)^3]\mathrm{d}^3\mathbf{k}$, by an elementary geometrical argument.

Let $N = \rho\nu$ be the number of electrons in volume $\nu$. These electrons occupy the N lowest Kohn-Sham spin orbitals, i.e., those with $k < k_F$:

$$N = 2\sum_{\mathbf{k}} \theta(k_F - k) = 2\frac{\nu}{(2\pi)^3} \int_0^{k_F} \mathrm{d}k\, 4\pi k^2 = \nu \frac{k_F{}^3}{3\pi^2}$$

where $k_F$ is called the Fermi wavevector. The Fermi wavelength $2\pi/k_F$ is the shortest de Broglie wavelength for the non-interacting electrons. Clearly

$$\rho = \frac{k_F{}^3}{3\pi^2} = \frac{3}{4\pi r_s{}^3}$$

where the Seitz radius rs is the radius of a sphere which on average contains one electron. The kinetic energy of an orbital is $k^2/2$, and the average kinetic energy per electron is

$$t_s(\rho) = \frac{2}{N}\sum_{\mathbf{k}} \theta(k_F - k)\frac{k^2}{2} = \frac{2\nu}{N(2\pi)^3} \int_0^{k_F} \mathrm{d}k\, 4\pi k^2 \frac{k^2}{2} = \frac{3}{5}\frac{k_F{}^2}{2}$$

In other notation,

$$t_s(\rho) = \frac{3}{10}(3\pi^2\rho)^{2/3} = \frac{3}{10}\frac{(9\pi/4)^{2/3}}{r_s{}^2}$$

**Thomas-Fermi Kinetic Energy Functional . . .**

The ground state energy of the Homogeneous Electron Gas (HEG) is a function of electron density alone. Imagine an infinite suspense of HEG, if we study a small chunk of it, say a box with side l, then we can solve the familiar particle in a periodic box problem and get

$$\epsilon_n = \frac{h^2}{2ml^2}n^2$$

In the grand scheme of things, we need to add up the energies of all such boxes of volume $dv = l^3$ to get the total energy of HEG. Thus let's say there are dN electrons in this region, then the Fermi level

$$2 \cdot \frac{4}{3}\pi n_F^3 = dN \Rightarrow n_F = (\frac{3dN}{8\pi})^{1/3}$$

The total energy of the particles inside is then

$$dE = 2 \cdot \int_0^{2\pi} \int_0^{\pi} \int_0^{n_F} \epsilon_n n^2 sin\theta \, dn \, d\theta \, d\phi = 8\pi \int_0^{n_F} \frac{h^2}{2ml^2}n^4 dn$$

$$= \frac{8\pi h^2}{10m}\frac{n_F^5}{l^2} = \frac{8\pi h^2}{10m}\frac{3}{8\pi}(\frac{3}{8\pi})^{2/3}\frac{dN^{5/3}}{l^2} = \frac{3h^2}{10m}(\frac{3}{8\pi})^{2/3}(\frac{dN}{dV})^{5/3}dV$$

$\because \rho = \frac{dN}{dV}$ is the density of electrons inside the box. Let $C_F = \frac{3h^2}{10m}(\frac{3}{8\pi})^{2/3}$, $\therefore$ the total energy (which is just kinetic energy) of HEG is

$$T(\rho) = \int dE = C_F \int \rho dV$$

While this is correct for HEG, it is not obvious if this relation will hold for inhomogeneous electron gas. Therefore Thomas and Fermi used *Local Density Approximation* (LDA), which says the properties of an inhomogeneous electron gas is locally identical to those of HEG. Thus they introduced the *Thomas-Fermi kinetic energy functional* -

$$T_{TF}[\rho] = \int dE = C_F \int \rho(\vec{r}) \, d\vec{r}$$

# Answer: 7 (C)

**Runge-Gross Theorem . . .**
*The time-dependent extension of the ordinary Hohenberg-Kohn theorem -*

**To demonstrate** - If two potentials, $v_s(\mathbf{r}, t)$ and $v_s'(\mathbf{r}, t)$, differ by more than a purely time-dependent function $c(t)$, they cannot produce the same time-dependent density, $\rho(\mathbf{r}, t)$, i.e. $v_s(\mathbf{r}, t) \neq v_s'(\mathbf{r}, t) + c(t) \Rightarrow \rho(\mathbf{r}, t) \neq \rho'(\mathbf{r}, t)$

Restricting to external potentials that are Taylor expandable with respect to the time coordinate around the initial time $t_0$,

$$v_s(\mathbf{r}, t) = \sum_{k=0}^{\infty} c_k(\mathbf{r})(t - t_0)^k$$

with the expansion coefficients

$$c_k(\mathbf{r}) = \frac{1}{k!} \frac{\partial^k}{\partial t^k} v_s(\mathbf{r}, t) \Big|_{t=t_0}$$

Furthermore define the function

$$u_k(\mathbf{r}) = \frac{\partial^k}{\partial t^k} [v_s(\mathbf{r}, t) - v'_s(\mathbf{r}, t)] \Big|_{t=t_0}$$

Clearly, if the two potentials are different by more than a purely time-dependent function, at least one of the expansion coefficients in their Taylor expansion around $t_0$ will differ by more than a constant

$$\exists_{k \geq 0} : u_k(\mathbf{r}) \neq constant \tag{1}$$

In the first step of the proof we demonstrate that if $v \neq v' + c(t)$, then the current densities, $j$ and $j'$, generated by $v$ and $v'$, are also different. The current density $j$ can be written as the expectation value of the current density operator:

$$j(\mathbf{r}, t) = \langle \Psi(t) | \hat{j}(\mathbf{r}) | \Psi(t) \rangle$$

where the operator $\hat{j}$ is

$$\hat{j}(\mathbf{r}) = -\frac{1}{2i} \left\{ \left[ \nabla \hat{\psi}'(\mathbf{r}) \right] \hat{\psi}(\mathbf{r}) - \hat{\psi}'(\mathbf{r}) \left[ \hat{\psi}(\mathbf{r}) \right] \right\}$$

Using the quantum-mechanical equation of motion, which is valid for any operator, $\hat{O}(t)$,

$$i \frac{\mathrm{d}}{\mathrm{d}t} \langle \Psi(t) | \hat{O}(t) | \Psi(t) \rangle = \langle \Psi(t) | i \frac{\partial}{\partial t} \hat{O}(t) + \left[ \hat{O}(t), \hat{H}(t) \right] | \Psi(t) \rangle$$

to write the equation of motion for the current density in the primed and unprimed systems,

$$i \frac{\mathrm{d}}{\mathrm{d}t} j(\mathbf{r}, t) = \langle \Psi(t) | \left[ j(\mathbf{r}), \hat{H}(t) \right] | \Psi(t) \rangle \tag{2}$$

$$i \frac{\mathrm{d}}{\mathrm{d}t} j'(\mathbf{r}, t) = \langle \Psi'(t) | \left[ j(\mathbf{r}), \hat{H}'(t) \right] | \Psi'(t) \rangle \tag{3}$$

As we start from a fixed initial many-body state, at $t_0$ the wave-functions, the densities, and the current densities have to be equal in the primed and unprimed systems

$$|\Psi(t)\rangle = |\Psi'(t)\rangle \equiv |\Psi_0\rangle$$

$$n(\mathbf{r}, t_0) = n'(\mathbf{r}, t_0) \equiv n_0(\mathbf{r})$$

$$j(\mathbf{r}, t_0) = j'(\mathbf{r}, t_0) \equiv j_0(\mathbf{r})$$

3

Taking the difference between the equations of motion (2) and (3) we obtain, at $t = t_0$,

$$i\frac{\mathrm{d}}{\mathrm{d}t}\left[j(\mathbf{r},t) - j'(\mathbf{r},t)\right]_{t=t_0} = \langle \Psi_0|\left[j(\mathbf{r}), \hat{H}(t_0) - \hat{H}'(t_0)\right]|\Psi_0\rangle$$
$$= \langle \Psi_0|\left[j(\mathbf{r}), v(\mathbf{r},t_0) - v'(\mathbf{r},t_0)\right]|\Psi_0\rangle \quad (4)$$
$$= in_0(\mathbf{r})\nabla\left[v(\mathbf{r},t_0) - v'(\mathbf{r},t_0)\right]$$

Let us assume that (1) is fulfilled already for k = 0, i.e. that the two potentials, $v$ and $v'$, differ at $t_0$. This immediately implies that the derivative on the left-hand side of (4) differs from zero. The two current densities $j$ and $j'$ will consequently deviate for $t > t_0$. If k is greater than zero, the equation of motion is applied k+1 times, yielding

$$\frac{d^{k+1}}{dt^{k+1}}\left[j(\mathbf{r},t) - j'(\mathbf{r},t)\right]_{t=t_0} = n_0(\mathbf{r})\nabla v_k(\mathbf{r}) \quad (5)$$

The right-hand side of (5) differs from zero, which again implies that $j(\mathbf{r},t) \neq j'(\mathbf{r},t)$ for $t > t_0$. This concludes the first step of the proof of the Runge-Gross theorem.

In a second step we prove that $j(\mathbf{r},t) \neq j'(\mathbf{r},t)$ implies $n \neq n'$. To achieve that purpose we will make use of the continuity equation -

$$\frac{\partial}{\partial t}n(\mathbf{r},t) = -\nabla \cdot j(\mathbf{r},t) \quad (6)$$

If we write (6) for the primed and unprimed system and take the difference, we arrive at

$$\frac{\partial}{\partial t}\left[n(\mathbf{r},t) - n'(\mathbf{r},t)\right] = -\nabla \cdot \left[j(\mathbf{r},t) - j'(\mathbf{r},t)\right]$$

As before, we would like an expression involving the kth time derivative of the external potential. We therefore take the (k+1)th time-derivative of the previous equation to obtain (at $t = t_0$)

$$\frac{\partial^{k+2}}{\partial t^{k+2}}\left[n(\mathbf{r},t) - n'(\mathbf{r},t)\right]_{t=t_0} = -\nabla \cdot \frac{\partial^{k+1}}{\partial t^{k+1}}\left[j(\mathbf{r},t) - j'(\mathbf{r},t)\right]_{t=t_0}$$

In the last step we made use of (5). By the hypothesis (1) we have $v_k(\mathbf{r}) \neq const$. Hence it is clear that if

$$\nabla \cdot \left[n_0(\mathbf{r})\nabla v_k(\mathbf{r})\right] \neq 0 \quad (7)$$

then $n \neq n'$, from which follows the Runge-Gross theorem. To show that (7) is indeed fulfilled, we use the versatile technique of demonstration by *reductio ad absurdum*. Let us assume that $\nabla \cdot \left[n_0(\mathbf{r})\nabla v_k(\mathbf{r})\right] = 0$ with $u_k(\mathbf{r}) \neq constant$, and look at the integral

$$\int d^3 r n_0(\mathbf{r})\left[\nabla v_k(\mathbf{r})\right]^2 = -\int d^3 r v_k(\mathbf{r})\nabla \cdot \left[n_0(\mathbf{r})\nabla v_k(\mathbf{r})\right] + \int_S n_0(\mathbf{r})v_k(\mathbf{r})\nabla v_k(\mathbf{r}) \cdot dS$$

This equality was obtained with the help of Green's theorem. The first term on the right-hand side is zero by assumption, while the second term vanishes if the density and the function $v_k(\mathbf{r})$ decay in a "reasonable" manner when $r \to \infty$. This situation is always true for finite systems. We further notice that the integrand $n_0(\mathbf{r})\left[\nabla v_k(\mathbf{r})\right]^2$ is always positive. These diverse conditions can only be satisfied if either the density $n_0$ or $\nabla v_k(\mathbf{r})$ vanish identically. The first possibility is obviously ruled out, while the second contradicts our initial assumption that $v_k(\mathbf{r})$ is not a constant. This concludes the proof of the **Runge-Gross theorem**.

# Answer: 8

**Action in the context of TDDFT . . .**
In static quantum mechanics, the ground-state of the system can be determined through the minimization of the total energy functional $E[\Phi] = \langle \Phi | \hat{H} | \Phi \rangle$

In time-dependent systems, there is no variational principle on the basis of the total energy for it is not a conserved quantity. ∃ However, a quantity analogous to the energy, the quantum mechanical action

$$A[\Phi] = \int_{t_0}^{t_1} dt \langle \Phi(t) | i\frac{\partial}{\partial t} - \hat{H}(t) | \Phi(t) \rangle \tag{8}$$

where $\Phi(t)$ is a N-body function defined in some convenient space.
From expression (8) it is easy to obtain two important properties of the action: i) Equating the functional derivative of (8) in terms of $\Phi^*(t)$ to zero, we arrive at the time-dependent Schrodinger equation. We can ∴ solve the time-dependent problem by calculating the stationary point of the functional $A[\Phi]$. The function $\Phi^*(t)$ that makes the functional stationary will be the solution of the time-dependent many-body Schrodinger equation. There is no "minimum principle", as in the time-independent case, but only a "stationary principle". ii) The action is always zero at the solution point, i.e. $A[\Psi] = 0$. These two properties make the quantum-mechanical action a much less useful quantity than its static counterpart, the total energy.

A time-dependent problem in quantum mechanics is mathematically defined as an initial value problem. This stems from the fact that the time-dependent Schrodinger equation is a first-order differential equation in the time coordinate. The wave-function (or the density) thus depends on the initial state, which implies that the Runge-Gross theorem can only hold for a fixed initial state (and that the xc potential depends on that state). In contrast, the static Schrodinger equation is a second order differential equation in the space coordinates, and is the typical example of a boundary value problem.

# Answer: 9

**Problem with the Action defined by Runge Gross . . .**
In their seminal paper, Runge and Gross approached the definition of the KS potential through an action-based argument starting from the Dirac action

$$A[\Psi] = \int_{t_0}^{t_1} dt \langle \Psi(t) | \hat{H}(t) - i\frac{\partial}{\partial t} | \Psi(t) \rangle$$

Treated as a functional of the wave function, $A[\Psi]$, variations of the wave function yield the many-body Schrödinger equation as the stationary point. Given the unique mapping between densities and wave function, Runge and Gross then treated the Dirac action as a density functional, $A[\rho] = A[\Psi[\rho]]$, and derived a formal expression for the exchange-correlation component of the action, which determines the exchange-correlation potential by functional

differentiation. Later it was observed that an approach based on the Dirac action yields paradoxical conclusions when considering the causality of the response functions it generates. The density response function, the functional derivative of the density with respect to the external potential, should be causal: a change in the potential at a given time can not affect the density at earlier times. The response functions from the Dirac action however are symmetric in time so lack the required causal structure. An approach which does not suffer from this issue was later introduced through an action based on the *Keldysh formalism* of complex-time path integration. An alternative resolution of the causality paradox through a refinement of the action principle in real time has been recently proposed by *Vignale*.

<u>In short</u> - *In ordinary DFT, $V_{xc}$ is normally written as a functional derivative of the xc energy. This follows from a variational derivation of the Kohn-Sham equations starting from the total energy. It is not straightforward to extend this formulation to the time-dependent case due to a problem related to causality.*

# Answer: 10 (C)

**Derivation of Born Oppenheimer approximation ...**

## Hamiltonian of the coupled electron-ion system

**N ions**  coordinates $\vec{R}_1,...,\vec{R}_N \equiv \vec{R}$, momenta $\vec{P}_1,...,\vec{P}_N \equiv \vec{P}$, charges $Z_1,...,Z_N$, masses $M_1,...,M_N$

$N_e$ **electrons**  coordinates $\vec{r}_1,...,\vec{r}_N \equiv \vec{r}$, momenta $\vec{p}_1,...,\vec{p}_N \equiv \vec{p}$, mass m

$$
\begin{aligned}
\hat{H} &= \sum_{I=1}^{N} \frac{\vec{P}_I^{\,2}}{2M_I} + \sum_{I>J} \frac{Z_I Z_J e^2}{|\vec{R}_I - \vec{R}_J|} + \sum_{i=1}^{N_e} \frac{\vec{p}_i^{\,2}}{2m} + \sum_{i>j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_{i,I} \frac{Z_I e^2}{|\vec{R}_i - \vec{r}_i|} \qquad (9) \\
&= T_N + V_{NN}(\vec{R}) + T_e + V_{ee}(\vec{r}) - V_{Ne}(\vec{r}, \vec{R})
\end{aligned}
$$

## The Schrödinger equation

$$
[T_N + V_{NN}(\vec{R}) + T_e + V_{ee}(\vec{r}) - V_{Ne}(\vec{r}, \vec{R})]\psi(x, \vec{R}) = E\psi(x, \vec{R}) \qquad (10)
$$

where $x \equiv (\vec{r}, s)$ is the full set of electronic positions and spin variables.

## Born-Oppenheimer approximation

Difference in time-scales of nuclear and electronic motions $\rightarrow$ *quasi-separable ansatz*

$$
\phi(x, \vec{R}) = \psi(x, \vec{R})\chi(\vec{R}) \qquad (11)
$$

where $\psi(x, \vec{R})$ is the electronic wave function, $\chi(\vec{R})$ is the nuclear wave function.

$\because \chi(\vec{R})$ is more localized than $\psi(x, \vec{R}) \therefore \nabla_I \chi(\vec{R}) >> \nabla_I \psi(x, \vec{R}) \longrightarrow$ *Decoupled adiabatic Schrödinger equations of electrons and nuclei.*

Thus making the *Adiabatic approximation*, of ions moving on the potential-energy surface of the electronic ground state $\varepsilon_0$, leads to time-independence in ion dynamics.

$$[T_e + V_{ee}(\vec{r}) - V_{Ne}(\vec{r}, \vec{R})]\psi(x, \vec{R}) = \varepsilon_0(\vec{R})\psi(x, \vec{R})$$

$$[T_N + V_{NN}(\vec{R}) + \varepsilon_0(\vec{R})]\chi(\vec{R}) = i\hbar\frac{\partial \chi(\vec{R})}{\partial t} \tag{12}$$

# Answer: 11

**N- and V-representability, Lieb-Levy constrained search formalism ...**
A V-representable density is a ground state density that can be associated with a Hamiltonian that has an external potential, $v(\vec{r})$. In the Hohenberg-Kohn theorems, one important assumption not mentioned is that, during the minimization, as we vary the density, we assume that it remains V-representable. It is, however, not clear that an arbitrary density, which integrates to an integer number of electrons, would be the ground state of a smooth external potential. **Example**: Any excited state density of single particles in finite systems.

In order to overcome the V-representability problem, a more general variational routine was proposed independently by **Levy and Lieb** in their respective pioneering works. Their extended minimization algorithm required the densities to be only N-representable. An N-representable density is one which can be derived from an antisymmetric wavefunction.

Redefining the universal part of the Hohenberg-Kohn energy functional, given a Hamiltonian $\hat{H} = \hat{T} + \hat{V}_{ee} + \sum_i \hat{v}_i$, F[n] was defined by Hohenberg and Kohn to be the sum of the kinetic and the electron-electron interaction energies. In the new definition of Levy and Lieb, the universal part of the energy functional

$$Q[n] = \min_{\Psi_n \to n} \langle \Psi_n | \hat{T} + \hat{V}_{ee} | \Psi_n \rangle \tag{13}$$

where a constrained minimization is conducted over all the antisymmetric wavefunctions $\Psi_n$, which yield the trial density n. With the definition in Eq. 13, we assume that the arbitrary trial density can be obtained from an antisymmetric wavefunction, in other words, is N-representable.

In order for Q[n] to be a valid universal function

**Theorem I** : For an arbitrary N-representable density n,

$$\int d\vec{r}\, \hat{v}(\vec{r})\, n(\vec{r}) + Q[n] \geq E_0 \tag{14}$$

where $\hat{v}$ is the one-body operator which constitutes the external potential

$$\hat{V}_{ext} = \sum_i \hat{v}(\vec{r}_i) \tag{15}$$

and $E_0$ is the ground state energy.

**Proof**: Following the notation of Levy in his PNAS paper, define $\Psi^n_{min}$ as the wavefunction that minimizes $\langle \Psi^n | \hat{T} + \hat{V}_{ee} | \Psi^n \rangle$ for a fixed n. Then by the definition in Eq. 13, we have

$$Q[n] = \langle \Psi^n_{min} | \hat{T} + \hat{V}_{ee} | \Psi^n_{min} \rangle \tag{16}$$

and in particular for the ground state density that we seek

$$Q[n_{gs}] = \langle \Psi^{n_{gs}}_{min} | \hat{T} + \hat{V}_{ee} | \Psi^{n_{gs}}_{min} \rangle \tag{17}$$

The minimum total energy for an arbitrary density, n (the left-hand side of the inequality in Eq. 14) is then given by

$$\int d\vec{r}\, \hat{v}(\vec{r})\, n(\vec{r}) + Q[n] = \int d\vec{r}\, \hat{v}(\vec{r})\, n(\vec{r}) + \langle \Psi^n_{min} | \hat{T} + \hat{V}_{ee} | \Psi^n_{min} \rangle \tag{18}$$

which can alternatively be expressed as

$$\int d\vec{r}\, \hat{v}(\vec{r})\, n(\vec{r}) + Q[n] = \langle \Psi^n_{min} | \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} | \Psi^n_{min} \rangle \tag{19}$$

making use of Eq. 15. Since, in the general case, the densitynin Eq. 19 is not the ground state density we have, by the variational principle,

$$\langle \Psi^n_{min} | \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} | \Psi^n_{min} \rangle \geq E_0 \tag{20}$$

Combining Eq. 19 and Eq. 20, we have

$$\int d\vec{r}\, \hat{v}(\vec{r})\, n(\vec{r}) + Q[n] \geq E_0 \tag{21}$$

which completes the proof of the first theorem.

**Theorem II** : For the ground state density,

$$\int d\vec{r}\, \hat{v}(\vec{r})\, n_{gs}(\vec{r}) + Q[n_{gs}] = E_0 \tag{22}$$

**Proof**: Relying on the considerations illustrated so far, the true ground state density of the system $\Psi_{gs}$ is not necessarily equal to the wavefunction that minimizes $Q[n_{gs}]$, i.e. $\Psi^{gs}_{min}$. As a result, the variational principle dictates that

$$\langle \Psi_{gs} | \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} | \Psi_{gs} \rangle \leq \langle \Psi^{gs}_{min} | \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} | \Psi^{gs}_{min} \rangle \tag{23}$$

Eq. 23 can be rewritten by separating the external potential energy term

$$\int d\vec{r}\, |\Psi_{gs}|^2\, \hat{v}(\vec{r}) + \langle \Psi_{gs} | \hat{T} + \hat{V}_{ee} | \Psi_{gs} \rangle \leq \int d\vec{r}\, \hat{v}(\vec{r})\, n_{gs}(\vec{r}) + \langle \Psi^{gs}_{min} | \hat{T} + \hat{V}_{ee} | \Psi^{gs}_{min} \rangle \tag{24}$$

which, making use of the fact that the first terms on both sidesgives the same result, can be reduced to

$$\langle \Psi_{gs} | \hat{T} + \hat{V}_{ee} | \Psi_{gs} \rangle \leq \langle \Psi^{gs}_{min} | \hat{T} + \hat{V}_{ee} | \Psi^{gs}_{min} \rangle \tag{25}$$

On the other hand, since both wavefunctions correspond to the same density, namely the ground state density, variational principle also dictates

$$\langle \Psi_{gs} | \hat{T} + \hat{V}_{ee} | \Psi_{gs} \rangle \geq \langle \Psi_{min}^{gs} | \hat{T} + \hat{V}_{ee} | \Psi_{min}^{gs} \rangle \tag{26}$$

The only way Eq. 25 and Eq. 26 can both be satisfied is if equality holds. In other words,

$$\langle \Psi_{gs} | \hat{T} + \hat{V}_{ee} | \Psi_{gs} \rangle = Q[n_{gs}] \tag{27}$$

Combined with the definition of the ground state energy using the true ground state wavefunction

$$E_0 = \int d\vec{r} \, \hat{v}(\vec{r}) \, n_{gs}(\vec{r}) + \langle \Psi_{gs} | \hat{T} + \hat{V}_{ee} | \Psi_{gs} \rangle \tag{28}$$

Eq. 27 yields

$$\int d\vec{r} \, \hat{v}(\vec{r}) \, n_{gs}(\vec{r}) + Q[n_{gs}] = E_0 \tag{29}$$

and completes the proof of the second theorem.

We have thus replaced the V-representability condition required by the Hohenberg-Kohn theorems by the much weaker and relaxed N-representability condition

# Answer: 12 (C)

**Definitions of a functional and a functional derivative ...**

## Functional

A functional is a rule for going from a function to a number: say F[f] where f(x) is a function (such a rule is also referred to as a mapping). In a manner of speaking, a functional is a function of which the variable is a function.

The expectation value $\langle \Psi | \hat{H} | \Psi \rangle$ of quantum chemistry is a functional; given $\Psi$ one gets a number from this prescription. Similarly with $\langle \Psi | \Psi \rangle$, so that the usual variational method of quantum chemistry, is the search for the minimum (or extremum) of a functional.

## Functional Derivative

The differential of a functional is the part of the difference $F[f + \delta f] - F[f]$ that depends on $\delta f$ linearly. Each $\delta f(x)$ may contribute to this difference, so for very small $\delta f$ we write,

$$\delta F = \int \frac{\partial F}{\partial f(x)} \delta f(x) \, dx, \tag{30}$$

where the quantity $\frac{\partial F}{\partial f(x)}$ is the functional derivative of F with respect to f at the point x. Equation (30) is the rule for operating on $\delta f(x)$ to give a number $\delta F$, and is the

extension to continuous variables of the formula for the total differential of a function $F(f_1, f_2, ...) : dF = \sum_i (\frac{\partial F}{\partial f_i}) \, df_i$

In general, given a functional $F[\rho] = \int f(x, \rho, \rho^{(1)}, \rho^{(2)}, ..., \rho^{(n)}) dx$, where $\rho^{(n)}(x) = d^{(n)} \rho(x)/dx^{(n)}$ and $\rho$ vanishes at the boundary of x. Then

$$\frac{\partial F}{\partial \rho(x)} = \frac{\partial f}{\partial \rho} - \frac{d}{dx} \left( \frac{\partial f}{\partial \rho^{(1)}} \right) + \frac{d^2}{dx^2} \left( \frac{\partial f}{\partial \rho^{(2)}} \right) - ... + (-1)^n \frac{d^n}{dx^n} \left( \frac{\partial f}{\partial \rho^{(n)}} \right) \tag{31}$$

where $\frac{\partial f}{\partial \rho}$, $\frac{\partial f}{\partial \rho^{(1)}}$, ... are partial derivatives: $\frac{\partial f}{\partial \rho^{(p)}}$ is taken holding $\rho^{(m)}$ constant, $m \neq p$

# Part II

# Answer: 1

## Excited-State Studies of Polyacenes: A Comparative Picture Using EOMCCSD, CR-EOMCCSD(T), Range-Separated (LR/RT)-TDDFT,TD-PM3, and TD-ZINDO [1]

**Review ...**
In this paper, the $L_a$ and $L_b$ vertical excitation energies were computed for the acenes ranging from anthracene toheptacene, using a broad spectrum of excited-state theoretical approaches. It was found that High accuracy coupled cluster calculations (CR-EOMCCST(T)) agree extremely well with experimental results for both states and thus serve as a baseline for validating the lower-level theories. Also, Global hybrid TDDFT (e.g, B3LYP) performed poorly for the $L_a$ state, whereas range-separated hybrid (RSH) TDDFT (e.g, CAM-B3LYP, LC-BLYP, etc) better described the ionic $L_a$ state, at a cost of lost accuracy for the $L_b$ state. Real-time RSH TDDFT visualization showed that the excited state charge densities were consistent with the predictions of perimeter free electron orbital (PFEO) theory, and the red-shifts of the excitations were due to particle-on-a-ring-like confinements. For the semiempirical methods, with proper parametrization, ZINDO rivaled range-separated hybrids in accuracy, at a fraction of the computational cost. These results suggest a multi tiered approach to modeling complicated acene derivatives, as well films and crystals of these molecules: high accuracy coupled cluster calculations validate RSH TDDFT calculations on small (perhaps pairs of) molecules, which in turn enable careful parametrization of semiempirical calculations capable of modeling large systems.

# References

[1] K. Lopata, R. Reslan, M. Kowalska, D. Neuhauser, N. Govind, and K. Kowalski. Excited-state studies of polyacenes: A comparative picture using eomccsd, cr-eomccsd(t), range-separated (lr/rt)-tddft, td-pm3, and td-zindo. *Journal of Chemical Theory and Computation*, 7(11), Nov 2011.