Ensemble-Density Functional Theory for Excited States

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Abstract

Fundamental aspects of the ensemble-density functional approach to the calculation of excited state energies are reviewed. Attention is given to the quasi-local density approximation for the equiensemble exchange-correlation energy functional. In particular, compared with experimental data, numerical results for the excitation spectrum of the Helium atom produce an estimate of the deviations introduced by that approximation.

1   Introduction

The ensemble approach, developed in the past decade, provides a simple extension of Density Functional Theory to excited states [1]. That approach, proposed originally by Theophilou [2], is analogous to Mermin's finite temperature formalism [3], which focuses attention on the grand-canonical density at temperature $\theta = 1/k_B\beta$:

$$\rho^\theta = \text{Tr}\left\{e^{-\beta H}\hat{\rho}\right\}/\text{Tr}\left\{e^{-\beta H}\right\}, \tag{1}$$

where $\hat{\rho}$ is the density operator and H the grand-canonical Hamiltonian for an interacting electron system in an external potential $v(r)$.

The (finite) ensemble theory likewise focuses attention on an average density, but its averaging involves a finite number M of states. Considering the *equiensemble*, for example, one defines the arithmetic average

$$\rho^M = \sum_{m=1}^{M} \langle m|\hat{\rho}|m\rangle/M, \tag{2}$$

where $|m\rangle$ is the mth eigenstate of H, counted in order of increasing energy E_m.

In analogy with the termal averages in the canonical ensemble, averaged physical properties can be defined in the finite ensemble. Of special interest are the average energies $\mathcal{E}^M$ $(M = 1, 2, \ldots)$, from which the eigenvalues of H can be obtained. Again taking the equiensemble as an example, we have

$$E_M = M\mathcal{E}^M - (M-1)\mathcal{E}^{M-1} = \mathcal{E}^{M-1} + M(\mathcal{E}^M - \mathcal{E}^{M-1}). \tag{3}$$

At the formal level, this simple relation (which has no analogue in the thermal ensemble) determines the excited state energies, for as shown below, the ensemble approach produces formally exact expressions relating the ensemble-averaged energies to the ensemble-averaged density and the single-particle eigenvalues of Kohn-Sham–like equations. At the practical level, this scheme nevertheless involves an essential difficulty, since the ensemble-density functional theory—like the ground-state and the thermal-ensemble theories— requires an approximation for exchange-correlation energy functional to become operative, and since the local density approximation (LDA), so convenient for the ground-state and the thermal functionals, is inappropriate for the finite-ensemble exchange-correlation energy functional [4].

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To overcome this difficulty, Kohn [4] has proposed a quasi-local density approximation (QLDA), obtained by identifying the equiensemble with the thermal ensemble. This paper, which briefly reviews the fundamentals of the ensemble-density approach, gives special attention to that approximate form for the exchange-correlation functional. In special, to consider a concrete application of the QLDA, we discuss numerical results for the excitation spectrum of the He atom. The calculated excitation energies are in fair agreement with the experimental results; an analysis of the deviations reveals two main sources of error: (i) like the LDA, the QLDA incorporates spurious self-interactions, and (ii) the accuracy of the QLDA fluctuates with M, so that relatively large errors are introduced in the subtraction on the right-hand side of Eq. (3). The former source can be easily neutralized, by measuring energies from the ionization threshold or by introducing self-interaction corrections analogous to Perdew's and Zunger's [5]. The latter is more resistant. To eliminate it, an alternative approximation would be necessary, but fortunately, it is not very serious, the deviations it introduces amounting to less than 20% of the energies measured from the ionization threshold.

Following these preliminary considerations, a recapitulation of the essential features of the finite-ensemble approach will be presented in Section 2. To keep the notation short, a non-degenerate spectrum is considered, the extension to arbitrary degeneracy being trivial. Section 3 discusses general aspects of the QLDA and Section 4 the results it produces for the He atom. Conclusions are summarized in Section 5.

2   Ensemble Method

The finite-ensemble approach is founded on a generalized Rayleigh-Ritz principle, applicable to excited states [6]. That principle states that, considered the Hilbert space $\mathcal{L}$ of the eigenstates of a Hamiltonian H, considered its M lowest-lying eigenvalues E_1, ..., E_M, an orthonormal set of M trial states $|\phi_1\rangle$, ..., $|\phi_M\rangle$, and M positive weights $w_1 \geq w_2 \geq \ldots w_M$, then

$$\sum_{m=1}^{M} w_M \langle \phi_m | H | \phi_m \rangle \geq \sum_{m=1}^{M} w_m E_m. \tag{4}$$

This principle has a number of special cases and corollaries; most notable among these are the Rayleigh-Ritz principle for equiensembles [7] and the

variational principle brought to light by Löwdin [8]. The reader is referred to the original papers for clear discussions of those two theorems and to Ref. 6 for the conditions under which the equality holds in (4).

On the basis of the variational principle for ensembles, it is straightforward [9] to establish a Hohenberg-Kohn theorem and a Kohn-Sham scheme for the ensemble density

$$\rho^W(r) = \sum_{m=1}^{M} w_m \langle m|\hat{\rho}|m\rangle / \sum_{m=1}^{M} w_m, \tag{5}$$

where the superscript W represents the set $\{w_1, w_2, \ldots, w_M\}$.

Practical considerations dictate two choices for this set of weights. Since the QLDA applies exclusively to the equiensemble, it is convenient to consider either equiensemble (*i.e.*, equal) weights or weights that reduce to the equiensemble in appropriate limits. In the former case, one chooses

$$w_1 = \ldots = w_M = 1/M, \tag{6}$$

and in the latter,

$$\begin{aligned}
w_1 = \ldots = w_{M-1} &= 1 - w/(M-1) \\
w_M &= w \qquad (0 \leq w \leq 1/M).
\end{aligned} \tag{7}$$

These definitions ensure that $\sum w_m = 1$, making superfluous the denominator on the right-hand side of Eq. (5). For $w = 0$ and for $w = 1/M$, Eq. (7) reduces to the equiensembles with multiplicities $M-1$ and M, respectively. We shall refer to this interpolation between neighboring equiensembles as the *fractional occupation* ensemble.

2.1   Kohn-Sham equations.

The single-particle Kohn-Sham equations for both ensembles, (6) and (7), have the same form:

$$\left\{ -\frac{\nabla^2}{2} + v_s[\rho^W](r) \right\} \varphi_j^W(r) = \epsilon_j^W \varphi_j^W(r), \tag{8}$$

Here the superscript on the single-particle energies ϵ_j^W and wavefunctions $\varphi_j^W(r)$ remind us that they depend on the weights w_m $(m = 1, \ldots, M)$. The

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single-particle potential is

$$v_s[\rho](r) = v(r) + \int \frac{\rho(r')}{|r - r'|}\, dr' + v_{xc}^W[\rho](r), \tag{9}$$

where as in the ground-state formalism,

$$v_{xc}^W[\rho](r) = \delta E_{xc}^W[\rho^W]/\delta \rho^W(r). \tag{10}$$

Given an expression for the exchange-correlation energy functional $E_{xc}^W[\rho]$, one can solve these equations self-consistently, the ensemble density obtained from the single-particle wavefunctions φ_j and eigenvalues ϵ_j as

$$\rho^W(r) = \sum_{m=1}^{M} w_m \sum_{j=1}^{\infty} f_{jm}|\varphi_j^W(r)|^2, \tag{11}$$

where f_{jm} is the occupation (zero or unity) of the jth orbital φ_j^W in the mth lowest-lying noninteracting (*i.e.*, Kohn-Sham) eigenstate.

2.2 Excitation energies.

Different procedures distinguish the calculation of excitation energies in the two ensembles. In the equiensemble method, after solving the Kohn-Sham Eqs. (8–11), one computes the enquiensemble energies $\mathcal{E}^M$, given by [9]

$$\begin{aligned}
\mathcal{E}^M &= \mathcal{E}_s^M - \frac{1}{2} \int \frac{\rho^M(r)\rho^M(r')}{|r - r'|}\, dr\, dr' \\
&\quad - \int \rho^M(r) v_{xc}[\rho^M](r) + E_{xc}^M[\rho^M],
\end{aligned} \tag{12}$$

where $\mathcal{E}_s^M = \sum_m w_m \sum_j f_{jm}\epsilon_j$ denotes the equiensemble energy for the *non-interacting* system. Once the ensemble energies $\mathcal{E}^M$ are found, Eq.(1) determines the excited-state energies.

In the fractional occupation method, a relation analogous to Eq.(12) can be derived [9]. It is nevertheless most convenient to differentiate this relation with respect to the weight w, defined in Eq.(7), which yields a more compact expression for the difference between two equiensemble energies [9]:

$$\mathcal{E}^M - \mathcal{E}^{M-1} = \mathcal{E}_s^M - \mathcal{E}_s^{M-1} + \frac{1}{M}\frac{\partial E_{xc}^W[\rho^W]}{\partial w}\bigg|_{\rho^W}, \tag{13}$$

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where the derivative with respect to w is taken at the fixed density ρ^W determined by solving the Kohn-Sham equations.

Particularly interesting is the form Eq.(13) takes when $M = 2$. In this case, $\mathcal{E}^M = (E_1 + E_2)/2$ and $\mathcal{E}^{M-1} = E_1$, so that Eq.(13) becomes

$$E_2 - E_1 = \epsilon_{N+1}^W - \epsilon_N^W + \left. \frac{\partial E_{xc}^W[\rho^W]}{\partial w} \right|_{\rho^W}, \tag{14}$$

where ϵ_N^W and ϵ_{N+1}^W are the energies of the highest occupied and of the lowest unoccupied levels in the noninteracting ground state, respectively.

For $w = 0$ one recovers the $M = 1$ equiensemble, *i.e.*, the ground state. With $w = 0$ Eq.(14) therefore relates the first excitation energy to the difference between single-particle eigenvalues of the *ground-state* Kohn-Sham equations. This shows that, in principle, one can determine the first excitation energy by solving the ground-state equations; the calculation of the optical-excitation gap in semiconductors, a long-standing problem in Density Functional Theory, can in principle be carried out by this procedure. In practice, however, an approximation for the last term on the right-hand side of Eq.(14) is required. Unfortunately, no such approximation is currently available.

In the opposite extreme, $w = 1/2$, one recovers the $M = 2$ equiensemble and the ensemble density $\rho^W(r)$ is the arithmetic average between the ground-state and the first excited-state densities. By substituting the ground-state exchange-only potential for the ensemble exchange-correlation potential in Eqs. (9) and (10) and by neglecting the last term on the right-hand side of Eq.(14) one obtains Slater's transition state prescription [10] for the calculation of the first excitation energy. This simple derivation of the transition state method shows that, to refine that time-honored procedure, one needs an improved approximation for the ensemble exchange-correlation energy functional. This topic is discussed next.

3   The Quasi-Local Density Approximation.

Even in the case of slowly varying densities, the LDA provides a poor approximation for the ensemble exchange-correlation energy functional. To show this, we consider an ensemble comprising a finite number M of states and recall that the Local Density Approximation associates a homogeneous

interacting electron gas with the non-homogeneous system one is generally interested in. Since the homogeneous system is infinite, for any $m \leq M$, the energies of the mth excited state and of the ground state in the homogeneous interacting electron gas are identical. It follows that, *in the LDA,* the ground-state and the ensemble exchange-correlation energy functionals are identical. The local density form is therefore clearly inadequate to describe systems of finite size, and a non-local form is required.

Kohn [4] has constructed a quasi-local density approximation by first identifying the equiensemble with the thermal ensemble and then applying the LDA to the latter. For equiensemble multiplicity M, the two ensembles are equivalent in the $M \to \infty$ limit. Thus, for large M, the thermal ensemble is expected to provide a good approximation to the equiensemble. This is confirmed by the numerical results in Section 4.

The two ensembles are identified by choosing the thermal-ensemble temperature θ to make identical the entropies of the two ensembles. If the entropy of the thermal ensemble is computed in a local density approximation, we have

$$\int \sigma^\theta[\rho^W](r)\,dr = k_B \ln M. \tag{15}$$

where following traditional notation, $\sigma^\theta[\rho^W](r)$ indicates the entropy per unit volume of the interacting system σ^θ for a homogeneous interacting system with density equal to the local density $\rho^W(r)$.

3.1   Exchange-correlation functionals.

Eq. (15) substitutes thermal averages for the equiensemble averages in the definition

$$E_{xc}^W[\rho] = E_v^W[\rho] - T_s^W[\rho] - \frac{1}{2}\int \frac{\rho(r)\rho(r')}{|r - r'|}\,dr\,dr' - \int \rho(r)v(r)\,dr, \tag{16}$$

of the equiensemble exchange-correlation energy functional, which can therefore be written

$$E_{xc}^W[\rho] = E_v^\theta[\rho] - T_s^{\theta_s}[\rho] - \frac{1}{2}\int \frac{\rho(r)\rho(r')}{|r - r'|}\,dr\,dr' - \int \rho(r)v(r)\,dr, \tag{17}$$

where a different temperature θ_s has been associated with the kinetic energy functional, because that functional refers to a non-interacting ensemble and

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thus must be identified with a thermal ensemble through the relation

$$\int \sigma_s^{\theta_s}[\rho^W](r)\,dr = k_B \ln M \tag{18}$$

(where σ_s is the entropy per unit volume for a *noninteracting* homogeneous gas), instead of Eq.(15).

With the usual definition of the thermal ensemble [11] exchange-correlation energy functional $E_{xc}^\theta[\rho]$, Eq.(17) can be written

$$E_{xc}^W[\rho] = E_{xc}^\theta[\rho] + T_s^\theta[\rho] - T_s^{\theta_s}[\rho]. \tag{19}$$

Now that all quantities on the right-hand side are thermal averages, one can take advantage of the LDA to write

$$E_{xc}^W[\rho] = \int e_{xc}^\theta[\rho](r)\,dr + \int \left\{ t_s^\theta[\rho](r) - t_s^{\theta_s}[\rho](r) \right\}\,dr, \tag{20}$$

where e_{xc}^θ and t_s^θ are the exchange-correlation and kinetic energy of an interacting and a noninteracting homogeneous systems at temperature θ, respectively. Finally, an approximation for the equiensemble exchange-correlation potential is easily obtained by functionally differentiating Eq.(20) with respect to $\rho(r)$, at fixed entropy. This yields

$$v_{xc}^W[\rho](r) = \mu^\theta[\rho](r) - \mu_s^\theta[\rho](r), \tag{21}$$

where μ^θ (μ_s^θ) represents the chemical potential of a homogeneous interacting (noninteracting) gas at the temperature θ.

3.2   Practical and operational aspects.

With Eqs. (15) and (18) defining the two temperatures θ and θ_s, practical computations of the equiensemble energy proceeds as follows. Given an initial approximation for the potential $v_s(r)$, one solves Eq.(8) and determines the single-particle wavefunctions and energies. From them, through Eq.(11), one computes the ensemble-averaged densities $\rho^W(r)$ and then the two temperatures, by solving numerically Eqs. (15) and (18). Eq.(21) then provides an approximation for the exchange-correlation potential on the right-hand side of Eq.(9) and the cycle can be repeated. Once self-consistency is reached within a pre-established accuracy, the resulting density is substituted in Eqs.

(12) and (20), thus determining the equiensemble energy in the equiensemble approach.

In the fractional occupation approach, an additional approximation is necessary to define the derivative on the right-hand side of Eq.(13). Since that derivative is taken at constant density, and since the only available approximation—the QLDA—covers exclusively the equiensemble, it is convenient to resort to the following finite-difference formula interpolating between the $M-1$-state (*i.e.*, $w = 0$) and the M-state ($w = 1/M$) equiensembles:

$$\frac{\partial E_{xc}^{w=1/2M}[\rho]}{\partial w} = M\left\{E_{xc}^{w=1/M}[\rho] - E_{xc}^{w=0}[\rho]\right\}. \qquad (22)$$

By choosing $w = 1/2M$ on the left-hand side, we reduce the error in this expression to $\mathcal{O}(1/M^2)$. The exchange-correlation potential $v_{xc}^{w=1/2M}$, needed to compute $\rho^{w=1/2M}$, is likewise determined by interpolation:

$$v_{xc}^{w=1/2M}[\rho](r) = \left\{v_{xc}^{w=1/M}[\rho](r) + v_{xc}^{w=0}[\rho](r)\right\}/2, \qquad (23)$$

again with an error of $\mathcal{O}(1/M^2)$. In the QLDA, the two equiensemble potentials on the right-hand side are given by Eq.(21).

The solution of the Kohn-Sham equations now proceeds as in the equiensemble method, and Eq.(22) determines the equiensemble energy differences.

The current status of the homogeneous electron gas problem, recently reviewed by Dandrea *et al.* [12], favors practical applications of both schemes. Expressions for the exchange-correlation energy are available [12, 13]; of these, the most accurate is the form proposed by Tanaka *et al.* [13], which has been employed in the numerical computation reported in Section 4.

4   Numerical Results.

Figure 1 displays equiensemble energies calculated in the equiensemble approach as a function of $1/\sqrt{M}$, to distribute more evenly the plotted data. The experimental energies, equiensemble averaged, are also shown. Although in fair agreement with the experimental values, the calculated $\mathcal{E}^M$ overestimate them systematically. Moreover, as $M \to \infty$, as indicated by the horizontal arrows pointing to the vertical axis, while the experimental values

tend to the ionization threshold, $E_{He^+}^{EXPT} = -4$Ry, the calculated ones tend to the LDA approximation, $E_{He^+}^{LDA} = -3.725$Ry. Since most of the discrepancy between these two threshold energies is due to the spurious self-interactions included in the LDA, the same self-interactions must respond for the discrepancy between the centered circles and the triangles in the figure.

This suggests that one add to the QLDA self-interaction corrections analogous to those of Perdew's and Zunger's [5]. An equally effective, if more primitive, solution is to compare the equiensemble energies measured from the LDA ionization threshold $E_{He^+}^{LDA}$ with the experimental averages reckoned from $E_{He^+}^{EXPT}$. As Table 1 shows, the agreement is then very good.

As expected, the agreement improves as M increases and the equivalence between the equiensemble and the thermal ensemble becomes more precise. The convergence to the experimental values in nonuniform, however. In fact, the percentual error in the table is a decreasing function of the number of angular momenta in the multiplet. Observing that a more complete set of angular momenta represents better the homogeneous gas, we associate this nonuniform convergence with the LDA in Eqs. (20) and (21).

Table 1 also compares the equiensemble energy *differences* calculated by the two ensemble approaches with the corresponding experimental values. While the remarkable agreement between the two methods indicates that the additional approximation in the fractional occupation approach affects insignificantly the accuracy of the calculation, the nonuniform convergence of the equiensemble energies to the experimental values is an important source of error in the calculated equiensemble energy differences. Through Eq. (3), this error is transmitted to the calculated excited-state energies. As a consequence, as Figure 1 shows, when compared with the experimental energies the excited-state energies calculated by either method display oscillatory errors with relatively large amplitude.

5   Conclusions

The quasi-local density approximation turns the ensemble-density functional formalism into a practical calculational procedure. The approximation is based upon the equivalence between the equiensemble and the thermal ensemble, exact in the limit of large ensemble multiplicity. Currently available expressions for the exchange-correlation energy of a homogeneous electron

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gas at finite temperature are sufficiently accurate to support practical implementations of the program.

The accuracy of the approximation is centrally limited by selfinteractions inherent in the local density approximation. Corrected for these interactions, the approximation yields equiensemble energies in good agreement with the experimental results. This agreement becomes more precise as the ensemble multiplicity grows, but depends on the number of angular momenta in each multiplet. The nonuniform accuracy affects perversely the accuracy of the equiensemble energy differences and consequently the accuracy of the calculated excited-state energies. In spite of this, of the limited number of electrons, and in spite of the rapidly varying density of the system here considered—the He atom—the agreement with the experimental excitation energies is fair.

References

[1] For reviews of Density Functional Theory including discussions of extensions to excited states, see R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989) and .

[2] A. K. Theophilou, J. Phys. C **12**, 5419 (1978); N. Hadjisavvas and A. K. Theophilou, Phys. Rev. A **32**, 720 (1985); A. K. Theophilou, in *The Single-Particle Density in Physics and Chemistry,* edited by N. H. March and B. M. Deb (Academic Press, New York, 1987), p. 201.

[3] N. D. Mermin, Phys. Rev. **137A**, 1441 (1965).

[4] W. Kohn, Phys. Rev. A **34**, 737 (1986).

[5] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[6] E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A **37**, 2805 (1988).

[7] R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience, New York, 1965), Vol. I, p. 459.

[8] P.-O. Löwdin in *Density Matrices and Density Functionals*, edited by R. Erdahl and V. H. Smith, Jr., (D. Reidel, 1987), p. 21.

[9] E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A **37**, 2809 (1988).

[10] J. C. Slater, *The Self-Consistent Field for Molecules and Solids* (McGraw-Hill, New York, 1974), Vol. IV, p. 51.

[11] For a review, see W. Kohn and P. Vashishta, in *Theory of the Inhomogeneous Electron Gas*, edited by S. Lundqvist and N. H. March (Plenum, New York, 1983), p. 79.

[12] R. G. Dandrea, N. W. Ashcroft, and A. E. Carlsson, Phys. Rev. B **34**, 2097 (1986).

[13] M. W. C. Dharma-wardana and R. Taylor, J. Phys. C **14**, 629 (1981); F. Perrot and M. W. C. Dharma-wardana, Phys. Rev. A **30**, 2619 (1984); S. Tanaka, S. Mitake, and S. Ichimaru, Phys. Rev. A **32**, 1896 (1985).

FIGURE CAPTIONS

1. Equiensemble energies calculated by the equiensemble approach (circles) compared with equiensemble averaged experimental energies (triangles) for the ensembles of He states indicated in Table I as functions of $1/\sqrt{M}$ where M is the ensemble multiplicity. The dashed lines guide the eye to the infinite-multiplicity limits, which coincide with the experimental and LDA ionization thresholds , respectively, indicated by the horizontal arrows pointing to the vertical axis.

2. Excited-state energies calculated in the equiensemble (solid lines)and fractional occupation (dashed lines) approaches, compared with the experimental energies in the He spectrum (bold lines). All energies have been averaged over spin, are subtracted from the ionization threshold (see text), and are classified by total electronic angular momentum.

Table 1: Equiensemble energies measured from $E_{He^+}^{LDA} = -3.725$Ry, and energy differences in the equiensemble (EQ) and fractional occupation (FO) approaches, compared with the experimental (EXPT) equiensemble energies, measured from $E_{He^+}^{EXPT} = -4.$Ry, and differences.

M	Highest Multiplet	$\mathcal{E}_M^{EXPT}$	$\mathcal{E}_M^{EQ}$	$\Delta\mathcal{E}_M^{EQ}$	$\Delta\mathcal{E}_M^{FO}$	$\Delta\mathcal{E}_M^{EXPT}$
1	1S	-1.807	-1.947(8%)			
5	2S	-0.630	-0.727(15%)	1.220	1.240	1.177
17	2P	-0.370	-0.386(4%)	0.341	0.346	0.260
21	3S	-0.325	-0.345(6%)	0.041	0.041	0.045
33	3P	-0.249	-0.265(6%)	0.081	0.083	0.077
53	3D	-0.197	-0.200(2%)	0.065	0.067	0.052
57	4S	-0.188	-0.192(2%)	0.008	0.008	0.009
69	4P	-0.166	-0.171(3%)	0.020	0.020	0.022
89	4D	-0.143	-0.146(2%)	0.025	0.024	0.023
117	4F	-0.124	-0.123(1%)	0.024	0.023	0.019
121	5S	-0.121	-0.120(1%)	0.002	0.002	0.003