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Dynamical Optimization for Partition Theory

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How to partition a chemical system into its constituent parts is a classic problem of theoretical chemistry. A formally exact solution has recently been developed, partition theory (PT), based on density functional theory [Cohen, M. H.; Wasserman, A. *J. Phys. Chem. A* **2007**, *111*, 2229]. PT presents a constrained optimization problem to which the Car−Parrinello (CP) method of electronic structure theory is well suited. We propose here a generalization of the CP method suitable for PT and thereby make way for its practical numerical implementation. We demonstrate that this CP implementation of PT need not increase the complexity of the computation of the system's electronic structure. The scheme provides an exact DFT formulation of, e.g., atoms in molecules theory that is amenable to numerical implementation.

I. Introduction

How to *partition* a molecule or larger aggregated system into smaller constituent parts is a classic problem of theoretical chemistry.[1] These parts may be acids, bases, sugars, monomers, side chains, etc. The many approximate or precise solutions proposed are not reviewed here. At the ultimate level of partition the general partition problem becomes the "atoms-in-molecules" problem with its own extensive literature which has been cogently reviewed by Nalewajski and Parr.[2]

In earlier papers, one of the current authors[3−5] has developed with Wasserman a formally exact procedure for the partition based on density-functional theory (DFT).[6] This partition theory (PT) fixes the nuclei of the parts in the positions they hold in the molecule and imposes the condition that the electron densities of the parts sum identically to that of the molecule. The average electron numbers of the parts are not restricted to integer values. Consequently, the ensemble formulation of DFT of Perdew et al. (PPLB) for noninteger systems must be used.[7,8] The partition theory was developed further as the foundation of a formulation of chemical reactivity theory (CRT)[5] free of the inconsistencies arising from derivatives of properties of reactants with respect to electron numbers in the original formulation of DFT-based CRT.[9,10] A very simple analytic illustration of PT has been worked out in quantitative detail.[11]

Finding the ground states of the parts is a constrained optimization problem like that of a typical electronic ground-state problem with a given nuclear configuration but with the added constraints that the electron densities of the parts add up to that of the molecule and that their electron numbers add up to the integer electron number of the molecule. In PT, a reactivity potential is introduced as a Lagrange multiplier of the density constraint and an internal chemical potential equal to the negative of the ionization potential of the molecule as that of the number constraint. For such constrained optimizations the Car−Parrinello (CP) method is ideal.[12,13] However, in the CP method as originally formulated, the Lagrange multipliers are adjusted at each iteration step. To do so for the reactivity potential would require at each step computation of a two-point susceptibility for each part, summing them, and inverting the sum, a prohibitively complex task.[14] Accordingly, we introduce here two modifications of the CP method. In the first, the reactivity potential is treated as a dynamical variable in parallel with the analogous treatment of the expansion parameters of the Kohn−Sham (KS) wavefunctions,[15] presuming prior knowledge of the molecular electron density and ionization potential. In the second, such prior knowledge is not required, and the ground-state properties of the molecule and of its parts emerge simultaneously as the iteration proceeds.

The paper is organized as follows. The partition theory is reviewed briefly in section II. The new, dynamical version of PT is described in section III for the case where prior knowledge of the molecular electron density $n_M(\mathbf{r})$ and of the molecular chemical potential μ_M exists. That version is generalized in section IV to the case where no prior information for the molecule exists; it allows the molecular and partition problems to be solved simultaneously. We conclude in section V with a discussion of the computational feasibility of the two methods.

II. Partition Theory

We consider an arbitrary molecule M in its ground state for a given atomic configuration. Let $n_M(\mathbf{r})$ be the electron density and the integer $N_M = \int n_M(\mathbf{r})\, d\mathbf{r}$ be the total number of electrons in the molecule. The corresponding ground-state energy E_M is, according to the Hohenberg and Kohn (HK) theorem,[6] a functional of $n_M(\mathbf{r})$, $E_M[n_M(\mathbf{r})]$, which is minimized by the actual ground-state density. We presently assume that we have solved the ground-state molecular problem; i.e., we know the nuclear configuration, $n_M(\mathbf{r})$ and the ground-state energy $E_M[n_M]$. We also know the chemical potential μ_M of the molecule, which is equal to minus the ionization potential of the molecule. The partition problem can be formulated as follows. "How can the total energy functional E_M be replaced by a sum of energy functionals $\tilde{E}_\alpha$ of constituent parts which can be used to a

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rigorous partition of the total charge density into a sum of semipositive definite partial densities $\tilde{n}_\alpha(\mathbf{r})$?" The partial densities do *not* necessarily integrate to integral numbers of electrons, i.e., the $\tilde{N}_\alpha = \int \tilde{n}_\alpha(\mathbf{r})\, d\mathbf{r}$ are in general not integers because the constituent parts interact among themselves. To solve this problem, we must *extend* the definition of the energy functional to systems with noninteger electron numbers. The correct way of doing that is by adopting the Perdew−Parr−Levy−Balduz (PPLB) ensemble density functional theory.[7,8] Following PPLB we write $\tilde{N}_\alpha = p_\alpha + \nu_\alpha$, where p_α is a *semipositive definite* integer and $0 < \nu_\alpha \leq 1$. The partial energy functional $\tilde{E}_\alpha$ is then given by the PPLB density functional of the part regarded as isolated but with its nuclear configuration identical to that in M,

$$\tilde{E}_\alpha = (1 - \nu_\alpha)E_\alpha[n_{p_\alpha}] + \nu_\alpha E_\alpha[n_{p_\alpha+1}] \tag{1}$$

The functional $\tilde{E}_\alpha$ has continuous piecewise linear dependence on $\tilde{N}_\alpha$ in consequence of the discrete convexity of the ground-state energy of integer bound systems.[5,7,8] The partition problem is then solved by minimizing $E_{\mathrm{PT}} = \sum_\alpha \tilde{E}_\alpha$ with the constraints $n_{\mathrm{M}}(\mathbf{r}) = \sum_\alpha \tilde{n}_\alpha(\mathbf{r})$, $N_{\mathrm{M}} = \sum_\alpha \tilde{N}_\alpha$. The present paper deals with how this can be done efficiently in practice.

According to KS, the molecular density can be represented as $n_{\mathrm{M}}(\mathbf{r}) = \sum_{i=1,N_{\mathrm{M}}} |\psi_i^{\mathrm{M}}(\mathbf{r})|^2$ in terms of single-particle orthonormal orbitals $\psi_i^{\mathrm{M}}(\mathbf{r})$. The functional E_{M} takes the form

$$E_{\mathrm{M}}[n_{\mathrm{M}}] = \frac{1}{2}\sum_i \int (\nabla\psi_i^{\mathrm{M}*})\cdot(\nabla\psi_i^{\mathrm{M}})\, d\mathbf{r} + \int V_{\mathrm{M}}(\mathbf{r},\mathbf{R}_{\mathrm{M}})\, n_{\mathrm{M}}(\mathbf{r})\, d\mathbf{r} + F[n_{\mathrm{M}}] \tag{2}$$

where $V_{\mathrm{M}}(\mathbf{r},\mathbf{R}_{\mathrm{M}})$ is the external potential of the nuclei, and $F[n_{\mathrm{M}}]$ is a universal functional of the density n_{M}. The KS construction allows us to replace the minimization of E_{M} with respect to the density $n_{\mathrm{M}}(\mathbf{r})$ with the minimization of E_{M} with respect to the $\psi_i^{\mathrm{M}}(\mathbf{r})$ subject to orthonormality constraints. For the parts, the KS prescription can be generalized to nonintegral electron numbers by defining:[4,5,7,8]

$$\tilde{n}_\alpha(\mathbf{r}) = (1 - \nu_\alpha)n_{p_\alpha}(\mathbf{r}) + \nu_\alpha n_{p_{\alpha+1}}(\mathbf{r})$$
$$n_p(\mathbf{r}) = \sum_{i=1,p} |\psi_i^p(\mathbf{r})|^2 \qquad p = p_\alpha, p_{\alpha+1} \tag{3}$$

Equations 3 require specification of the orthonormal orbitals $\psi_i^p(\mathbf{r})$ for the integer $p = p_\alpha$ and for $p = p_\alpha + 1$ and of the noninteger occupation number components ν_α. Thus, varying (p_α,ν_α) is equivalent to varying $\tilde{N}_\alpha$. The generalized minimization problem for E_{PT} with respect to the variables $\psi_i^p(\mathbf{r})$ $p = p_\alpha$ and $p = p_\alpha + 1$ and $\tilde{N}_\alpha$ is thus subject to the constraints

$$\int \psi_i^{p*}(\mathbf{r})\, \psi_j^p(\mathbf{r})\, d\mathbf{r} = \delta_{ij} \tag{4}$$

$$\sum_\alpha \tilde{N}_\alpha = N_{\mathrm{M}} \tag{5}$$

$$\sum_\alpha \tilde{n}_\alpha(\mathbf{r}) = n_{\mathrm{M}}(\mathbf{r}) \tag{6}$$

Using the technique of Lagrange multipliers, this is equivalent to finding the infimum[16] of the functional $G_{\mathrm{PT}}[\{n_p(\mathbf{r})\},\{p_\alpha,\nu_\alpha\}]$ given by

$$G_{\mathrm{PT}}[\{n_p\},\{p_\alpha,\nu_\alpha\}] = E_{\mathrm{PT}}[\{n_p\},\{p_\alpha,\nu_\alpha\}] - \sum_\alpha \sum_{p=p_\alpha,p_\alpha+1} \sum_{i,j=1}^{p} \lambda_{ij}^p \left(\int \psi_j^{p*}(\mathbf{r})\, \psi_i^p(\mathbf{r})\, d\mathbf{r} - \delta_{ij}\right) - \mu_{\mathrm{R}}\left(\sum_\alpha \tilde{N}_\alpha - N_{\mathrm{M}}\right) + \int V_{\mathrm{R}}(\mathbf{r})\left(\sum_\alpha \tilde{n}_\alpha(\mathbf{r}) - n_{\mathrm{M}}(\mathbf{r})\right) d\mathbf{r} \tag{7}$$

Here E_{PT} is given explicitly by

$$E_{\mathrm{PT}} = \sum_\alpha \{(1 - \nu_\alpha)E_\alpha[n_{p_\alpha}] + \nu_\alpha E_\alpha[n_{p_\alpha+1}]\} \tag{8}$$

and the KS form is used for $E_\alpha[n_p]$

$$E_\alpha[n_p] = \frac{1}{2}\sum_{i=1}^{p} \int (\nabla\psi_i^{p*})\cdot(\nabla\psi_i^p)\, d\mathbf{r} + \int V_\alpha n_p\, d\mathbf{r} + F[n_p] \qquad p = p_\alpha, p_\alpha + 1 \tag{9}$$

where V_α is the external potential of the nuclei of part α in their positions in M. In eq 7 λ_{ij}^p, $V_{\mathrm{R}}(\mathbf{r})$, and μ_{R} are Lagrange multipliers that impose the constraints (4)−(6), respectively. We call $V_{\mathrm{R}}(\mathbf{r})$ the *reactivity potential*.[3−5] It acts as an external potential on the electron density $\tilde{n}_\alpha(\mathbf{r})$ to impose the condition $\sum_\alpha \tilde{n}_\alpha(\mathbf{r}) = n_{\mathrm{M}}(\mathbf{r})$ and serves as a proxy for the mutual interaction of the various fragments. We also require that the chemical potential μ_R is fixed and equal to μ_{M},[4,5] i.e., the known chemical potential of the molecule; the corresponding term in eq 7 simply says that each fragment experiences the same chemical potential.

Note that $\tilde{E}_\alpha[n_p, p_\alpha, \nu_\alpha]$, eq 1, is the exact KS functional of part α. It has the correct derivative discontinuinities at integer $\tilde{N}_\alpha$, i.e., at $\nu_\alpha = 0, 1$. Although approximate functionals can be used for the individual components of $\tilde{E}_\alpha$, $E_\alpha[n_{p_\alpha}]$ and $E_\alpha[n_{p_\alpha+1}]$ having integer electron numbers, the continuation of such approximate functionals to a noninteger number should not be used for $\tilde{E}_\alpha$. Otherwise, a risk of substantial loss of accuracy could result.

In the conventional Car−Parrinello (CP) minimization procedure, imposing the orthonormalization of the $\psi_i^p(r)$ by calculating the Lagrange multipliers λ_{ij}^p does not pose particular difficulties.[13] On the other hand, calculating the reactivity potential via that methodology is impractical because it would require calculating an electronic response function (an inverse susceptibility) each time that the constraint (6) is imposed during CP iterations. We therefore regard eq 7 as a Legendre transformation from the variables $(\{\psi_i^p(\mathbf{r})\}, \{p_\alpha, \nu_\alpha\})$, constrained by eqs 5 and 6, to the variables $(\{\psi_i^p(\mathbf{r})\}, \{p_\alpha, \nu_\alpha\}, V_{\mathrm{R}}(\mathbf{r}))$ of which only the $\{\psi_i^p(\mathbf{r})\}$ are constrained (by eq 4). Optimization of the PT functional $G_{\mathrm{PT}}[(\{\psi_i^p(\mathbf{r})\}, \{p_\alpha, \nu_\alpha\}, V_{\mathrm{R}}(\mathbf{r}))]$ in eq 7 supplemented only by the orthonormality constraints is *equivalent* to the optimization of the same functional supplemented by the constraints (4)−(6). We use the phrase optimization of G_{PT} for the search of its stationary point because the latter is a saddle point, minimal with respect to the ψ but maximal with respect to V_{R}, as discussed further in section III.

An initial choice of $\{p_\alpha\}$ must be made before iteration on the values of the ψ_i^p and ν_α can start. They can be chosen via conventional chemical arguments, e.g., the anticipated formal oxidation states of the parts. For a given initial choice, no minimum may be found as the ν_α vary. Instead, an infimum could be found with respect to one or more ν_α at the end points 0 or 1 of their ranges. If found for $\nu_\alpha \uparrow 1$, that p_α has to be increased by one and the search resumed. If $\nu_\alpha \downarrow 0$, that p_α is to be decreased by one and the search resumed.

Next we discuss a strategy to optimize G_{PT} based on dynamical equations of motion which constitutes a generalization of conventional CP theory.[12,13] In particular, we consider in the next section the case in which the molecular density $n_M(\mathbf{r})$ is known, and the case in which the molecular density is unknown is considered in the subsequent section. In the latter case, the dynamical optimization is used to generate *simultaneously* the density of the parts and of the molecule.

III. Dynamical Optimization of the PT Functional; Molecular Density Known

Dynamical minimization of the KS energy functional was introduced in (12). This approach can be naturally extended to the PT functional G_{PT}, the derivatives of which with respect to the variables ($\{\psi_i^p(\mathbf{r})\}$, $\{p_\alpha, \nu_\alpha\}$, $V_R(\mathbf{r})$) can be easily calculated. We discuss here the particularly simple case of optimization by steepest descent/ascent (SAD) dynamics. Generalization to more efficient optimization schemes, such as damped molecular dynamics[13] and, even better, conjugate gradient dynamics,[17−20] is straightforward and will be discussed in a future paper on the numerical implementation of the PT methodology.

Given a generalized functional $\mathscr{F}[\{\mathscr{X}\}]$ depending on a set of fields $\{\mathscr{X}\}$, SAD optimization amounts to solving numerically the following set of ordinary first-order differential equations in a fictitious time variable:

$$\Gamma_i \dot{\mathscr{X}}_i = -\frac{\delta \mathscr{F}}{\delta \mathscr{X}_i} \tag{10}$$

In eq 10 Γ_i is a member of a set of friction coefficients that control the SAD dynamic response of the variables $\{\mathscr{X}\}$. Numerically, eq 10 is solved by finite differences in time starting from an initial guess $\{\mathscr{X}\}$ ($t = 0$). The trajectory generated by eq 10 approaches a stationary point $\{\mathscr{X}\}^0$ at sufficiently large t when $\delta\mathscr{F}/\delta\{\mathscr{X}\} \rightarrow 0$, signaling, for example, that the system approaches a saddle point of $\mathscr{F}$ located on the separatrix of the basin of the initial guess. The stationary point $\{\mathscr{X}\}^0$ does not depend on the parameters $\{\Gamma\}$, which are free to be chosen to speed up convergence.

Application of the SAD optimization procedure to the partition problem leads to the following equations:

$$\Gamma_{\psi^p}\dot{\psi}_i^p(\mathbf{r}) = -[(1-\nu_\alpha)\{(H^p_{KS}+V_R)\psi_i^p(\mathbf{r}) - \sum_j \lambda_{ij}^p \psi_j^p(\mathbf{r})\}]\delta_{p,p_\alpha} - [\nu_\alpha\{(H^p_{KS}+V_R)\psi_i^p(\mathbf{r}) - \sum_j \lambda_{ij}^p \psi_j^p(\mathbf{r})\}]\delta_{p,p_\alpha+1} \tag{11}$$

$$\Gamma_{V_R}\dot{V}_R(\mathbf{r}) = -[\sum_\alpha \tilde{n}_\alpha(\mathbf{r}) - n_M(\mathbf{r})] \tag{12}$$

$$\Gamma_{\nu_\alpha}\dot{\nu}_\alpha = -[E^R[n_{p_\alpha+1}] - E^R[n_{p_\alpha}] - \mu_M] = -[\mu_\alpha^R - \mu_M] \tag{13}$$

$$E^R[n_p] = E[n_p] + \int V_R(\mathbf{r})\, n_p(\mathbf{r})\, d\mathbf{r} \tag{14}$$

Equation 11 resembles the usual equation for SAD minimization of the KS functional in conventional CP theory.[13] H^p_{KS} is the KS Hamiltonian of part α depending on the set of orbitals $\{\psi_i^p\}$ with $p = p_\alpha$ or $p = p_\alpha + 1$. However, the presence of V_R in G_{PT}, augmenting the nuclear electrostatic potential in its dependence on $\sum_\alpha \tilde{n}_\alpha$, forces an interesting change. As G_{PT} is minimal with respect to the ψ_i^p, Γ_{ψ_p} must be positive so that integrating eq 11 over time forces the steepest *descent* in the ψ_i^p subspace. Similarly, G_{PT} is convex with respect to the ν_α, as its Hessian in the ν_α subspace is just the hardness matrix $\eta_{\alpha\beta}$ defined in (5), which is positive definite. On the other hand, as V_R is an external potential, G_{PT} is concave with respect to it, so Γ_{V_R} must be negative to enforce steepest *ascent* toward the stationary point, a maximum in the subspace containing V_R and orthonormal ψ_i^p. The Hessian of G_{PT} there is simply

$$\frac{\delta^2 G_{PT}}{\delta V_R(\mathbf{r})\, \delta V_R(\mathbf{r}')} = -\chi_R \tag{15}$$

where χ_R is a positive-definite susceptibility defined in ref 5 as

$$\chi_R = \sum_\alpha \chi_\alpha \tag{16}$$

$$\chi_\alpha = (1-\nu_\alpha)\chi_{p_\alpha} + \nu_\alpha \chi_{p_\alpha+1} \tag{17}$$

$$\chi_p = -\frac{\delta n_p}{\delta V_{ext}} \tag{18}$$

V_{ext} can be any external potential, V_R for example. Each χ_p is positive definite, and so therefore are χ_α and χ_R via (17) and (16). G_{PT} is therefore concave with respect to V_R, as stated above. The stationary point is a saddle point, and the search for it is an optimization in the general sense, not a minimization of G_{PT}. Moreover, the stationary point is unique because G_{PT} is everywhere concave with respect to V_R, and the $E^R[n_p]$ have unique minima and by conjecture[5] their ensemble possesses discrete convexity for given V_R. One can illustrate that uniqueness by integrating eqs 11−13 over successive small time intervals and observing that the resulting increments always move the system toward the sole stationary point.

Finally, we note that in eq 13, the chemical potential μ_α^R of α in the presence of V_R is taken as the difference in the total energies E^R. If the density functionals employed in actual computations were exact, this difference would be identical to the corresponding KS HOMO eigenvalue for $p_\alpha + 1$. However, for small systems like the parts, inaccuracies in the usual approximate density functionals can cause the KS HOMO to differ significantly from the total energy difference, which, in fact, gives a better approximation than the KS HOMO to the ionization energy. Nevertheless, of the two choices for μ_α^R, the KS HOMO in the presence of V_R must be used. The asymptotic behavior of the density of each part α is controlled by the KS HOMO eigenvalue of $p_\alpha + 1$ in the presence of V_R. Similarly, the asymptotic behavior of n_M is controlled by the KS HOMO eigenvalue of M. The constraint (6), as imposed through the evolution of V_R via eq 12, enforces the equality of the KS HOMO eigenvalue for each part α with that of M. Consequently, it is the KS HOMO eigenvalues of the parts that must be used for the μ_α^R in eq 13, and not the difference in total energies $E^R_{p_\alpha+1} - E^R_{p_\alpha}$, and similarly for M, when approximate density functionals are used. However, the usual care should be taken to avoid the introduction of multiple minima by such approximations.

The Lagrange multipliers that impose orbital orthonormality in (11) are calculated in the usual way.[12,13] For each part α, eq 11 amounts to computing two different SAD trajectories, one for the set of orbitals $\{\psi_i^{p_\alpha}\}$ and one for the set of orbitals $\{\psi_i^{p_\alpha+1}\}$. If the integer numbers p_α do not vary during SAD minimization, i.e., only the fractional occupations ν_α change, eqs 11−13 solve completely the optimization problem of PT. A special problem arises when the numbers p_α increase or decrease by a unit in the course of SAD minimization, as discussed above. This situation can be dealt with by adding S_p supplementary orbitals $\psi^p_{k=p+1,p+S_p}$ to the orbitals $\psi^p_{i=1,p}$ that are used to define the starting point of the SAD trajectory. The supplementary orbitals do not enter in the definition of the electron density $n_p(\mathbf{r})$, on which the KS Hamiltonian $H^p_{\rm KS}$ depends. They evolve as virtual orbitals; i.e., they follow an SD trajectory determined by the KS Hamiltonian $H^p_{KS} + V_{\rm R}$ and are subject to the constraint of orthogonality to the occupied orbitals $\psi^p_{i=1,p}$ and to the constraint of orthonormality among themselves. Whenever, during a trajectory, a p increases by unity, the virtual orbital corresponding to the lowest unoccupied KS eigenvalue becomes an occupied orbital and begins to contribute to the electronic density $n_p(\mathbf{r})$. At the same time the set of virtual orbitals is reduced by a unit. Correspondingly, whenever a p decreases by unity, the set of virtual orbitals increases by a unit. This procedure entails derivative discontinuities in the SAD trajectory. The discontinuities in the quantities themselves are however small because when an empty orbital starts to become occupied or a filled orbital starts to empty the resulting change of the electron density is very small.

IV. Dynamical Optimization of the PT Functional; Molecular Density Unknown

Absent PT, obtaining the molecular density $n_{\rm M}$ for a given nuclear configuration $\{\mathbf{R}_\alpha\}$ via the CP method using SD dynamics requires solving the standard CP equation by iteration,

$$\Gamma_{\psi_i{\rm M}}\dot{\psi}_i^{\rm M} = -H^{\rm M}_{\rm KS}\psi_i^{\rm M} + \sum_j \lambda_{ij}^{\rm M}\psi_j^{\rm M} \qquad (19)$$

with the result that at the stationary point,

$$\mu_{\rm M} = \epsilon^{\rm M}_{\rm M} \qquad (20)$$

where the symbols in eqs 19 and 20 take on their standard meanings, $\epsilon^{\rm M}_{\rm M}$ in particular being the KS HOMO eigenvalue. In eq 20, we deliberately use the KS HOMO of M instead of the ground state energy difference $E_{\rm M}(N_{\rm M}) - E_{\rm M}(N_{\rm M} - 1)$ in accord with the above discussion of the consequences of inaccuracy in the density functional $E_{\rm M}[n_{\rm M}]$. The density $n_{\rm M}$ has the standard form

$$n_{\rm M} = \sum_i^{\rm M} |\psi_i^{\rm M}|^2 \qquad (21)$$

Equations 19 and 11−13 are to be solved in parallel by iteration, using at a given stage of iteration of eqs 11−13 appropriate intermediate values of $n_{\rm M}$ from eq 21 and $\mu_{\rm M}$ from eq 20 as the values of $n_{\rm M}$ and $\mu_{\rm M}$ in eqs 11−13. How close the iteration of eqs 11−13 has to track the evolving value of $\mu_{\rm M}$ and $n_{\rm M}$ remains to be investigated. When iteration of both equations is complete, ground-state values for both the parts and the whole will have been found.

So far we have assumed that the nuclear coordinates $\{\mathbf{R}_\alpha\}$ are fixed. It would be straightforward to allow for nuclear relaxation by extending the optimization procedure also to the nuclear coordinates as done in the standard CP approach.[12,13]

V. Discussion

In ref 5 PT has already proved its worth in providing a sound foundation for chemical reactivity theory. At issue is whether, in regard to CRT, computation of the reactivities defined in ref 5 is feasible. Also, given the immense effort poured into the atoms in molecules theory (AIMT), now subsumed within PT, it is reasonable to expect further conceptual advances from PT. Remaining at issue, then, is whether quantitative results can be obtained with PT, for example values of the reactivities defined in ref 5. In the present paper, we have worked out modifications of the standard CP formalism for the cases $n_{\rm M}$ and $\mu_{\rm M}$, known or unknown. Thus whether PT can be made quantitative devolves to the computational complexity of these procedures.

There are A parts and each part has two components. Treating the parts as having the same size N for the first case, $n_{\rm M}$ known, the computational complexity of the partition scales as $2AN^3$ *if the presence of* V_R *does not significantly delocalize the* ψ^p_i, because computing $V_{\rm R}$ and the ν_α does not add significant computational complexity. The complexity of getting $n_{\rm M}$ and the $\{\mathbf{R}_\alpha\}$ by an ordinary CP computation scales as $(AN)^3$. The ratio of the two complexities is $2A^{-2}$. With A significant for large systems, carrying out the partition does not add significantly to the computational complexity of the original study of M. This conclusion does not change if the partition and finding $n_{\rm M}$ and $\{\mathbf{R}_\alpha\}$ are carried out simultaneously, the second case.

We conclude that PT is computationally feasible for all systems to which the ordinary CP method can be usefully applied and in which the presence of $V_{\rm R}$ does not delocalize $\tilde{n}_\alpha$. When that condition is violated, one must carry out $(2A + 1)$ computations of complexity $(AN)^3$, severely limiting the size of the systems which can be embraced by PT. Determining whether delocalization is introduced by $V_{\rm R}$ is thus a pressing issue for PT. The nearsightedness concept[21,22] suggests, however, that $V_{\rm R}$ probably does not delocalize the n_α in the general case.

There is an alternative to the PPLB form of $\tilde{E}_\alpha$ of eq 1, a continuous interpolation of $E_\alpha[n_p]$ of eq 9 between p_α and $p_\alpha + 1$.[23,24,25] Using such a form for $\tilde{E}_\alpha$ would reduce the number of ψ_i by a factor of ∼2, but at the cost of significant loss of accuracy in the density functional. Added to the existing inaccuracies of the density functionals for the integer number is the inaccuracy of the very complex mapping of the PPLB ensemble DF into a functional of a single density with noninteger number. For now, PPLB is preferred.

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