Dirichlet Boundary Conditions and Effect of Confinement on Chemical Reactivity

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To understand the source of discrepancy in the qualitative trends in the reactivity of the spherically confined atoms/ions when the high pressure is generated through the use of a proper Dirichlet boundary condition [*J. Chem. Sci.* **2005**, *117*, 379; *Phys. Chem. Chem. Phys.* **2008**, *10*, 1406] and of a cutoff function [*Chem. Phys. Lett.* **2003**, *372*, 805; *J. Phys. Chem. A* **2003**, *107*, 4877], a modified Herman−Skilman program is run. Results obtained from different formulas of reactivity parameters are analyzed. Change in reactivity for different electronic configurations is also reported. It is observed that the use of different formulas is the major source of discrepancy and not the Dirichlet condition, although the latter is highly recommended. As the cutoff radius of the confining spherical box decreases, the energy of the atom/ion increases, the electronegativity decreases, and the hardness increases and ultimately slightly decreases in an ultraconfined situation. For small R_C values, softness decreases and electrophilicity increases and attains relatively small values. The reactivity of confined atoms/ions is put in a proper perspective.

1. Introduction

The effect of spherical confinement on the chemical reactivity of many-electron systems has been studied in recent years.[1−4] Quantization is the effect of boundary, and hence the use of the proper boundary condition is important in quantum mechanics. Nonrelativistic Hartree−Fock−Slater calculations have been performed[1,2] to study the confined atoms/ions, where the boundary condition has been implemented via a cutoff function method and the reactivity parameters have been calculated using appropriate density functional quantities. Nonrelativistic spin-polarized Kohn−Sham equations with the Perdew−Wang exchange-correlation potential have been solved, and the energies of N- and $(N \pm 1)$-electron systems have been used in ref 3, and a potential barrier approach has been used wherein the energies of the frontier molecular orbitals have been used in ref 4. The Dirichlet boundary condition has been used in both of these papers. It may be noted that there hardly exists any result until date on the reactivity of confined many-electron systems with quantitative accuracy. To understand the chemical aspects of confinement, readers may look into the ref 4b and the special issue of *Phys. Chem. Chem. Phys.* on “Molecules in Confined Spaces” where it has appeared. Global reactivity descriptors such as electronegativity[5−7] (χ), hardness[8−11](η), and electrophilicity[12−14](ω) have been defined within a conceptual density functional theory[15−18](CDFT)-based framework. For an N-electron system with total energy E, electronegativity[7] (χ) and hardness[11](η) have been defined as

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(\mathbf{r})} \tag{1}$$

and

$$\eta = \frac{1}{S} = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\mathbf{r})} = \left(\frac{\partial \mu}{\partial N}\right)_{v(\mathbf{r})} \tag{2}$$

In eqs 1 and 2, μ is the chemical potential (Lagrange multiplier associated with the normalization constraint in DFT[19]), $v(\mathbf{r})$ is the external potential, and S is the softness.

The global electrophilicity index[12] (ω) has been defined as

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta} \tag{3}$$

A finite difference approximation to eqs 1 and 2 would yield

$$\chi = -\mu = \frac{I + A}{2} \tag{4}$$

and

$$\eta = I - A \tag{5}$$

where I and A are the ionization potential and the electron affinity, respectively.

One may obtain χ and η starting from the expression of the energy functional of DFT[19] as

$$E[\rho(\mathbf{r})] = F[\rho(\mathbf{r})] + \int \rho(\mathbf{r})v(\mathbf{r})\,d\mathbf{r} \tag{6}$$

where $F[\rho(\mathbf{r})]$ is the Hohenberg−Kohn universal functional of the electron density $\rho(\mathbf{r})$. A local density form of $F[\rho]$ was previously used as[1,2]

$$F[\rho] = C_K\int \rho^{5/3}\,d\mathbf{r} - \frac{1}{40}\int \frac{\mathbf{r}\cdot\nabla\rho}{r^2}\,d\mathbf{r} - C_X\int \rho^{4/3}\,d\mathbf{r} - \int \frac{\rho}{9.81 + 21.437\rho^{-1/3}}\,d\mathbf{r} + \frac{1}{2}\iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}' \tag{7}$$

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where $C_K = (^3/_{10})\,(3\pi^2)^{2/3}$ and $C_X = (^3/_4)\,(^3/_\pi)^{1/3}$. The above expression comprises functionals related to a first-order gradient-corrected Thomas−Fermi kinetic energy, Dirac exchange energy, a Wigner-type local correlation energy, and the classical Coulomb repulsion energy. A second-order functional derivative of $F[\rho(\mathbf{r})]$ provides a hardness kernel[20] as

$$\eta(\mathbf{r},\mathbf{r}') = \frac{\delta^2 F[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \qquad (8)$$

which may be used to calculate the global hardness as[20]

$$\eta = \frac{1}{N}\iint \eta(\mathbf{r},\mathbf{r}')f(\mathbf{r}')\rho(\mathbf{r})\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}' \qquad (9)$$

where $f(\mathbf{r})$ is the Fukui function given by[21]

$$f(\mathbf{r}) = \left(\frac{\partial\rho(\mathbf{r})}{\partial N}\right)_{v(\mathbf{r})} = \left(\frac{\partial\mu}{\partial v(\mathbf{r})}\right)_N \qquad (10)$$

Within a local model prescribed by Fuentealba,[22] $f(\mathbf{r})$ may be calculated using the local softness, $s(\mathbf{r})$ expressed in terms of $\eta(\mathbf{r},\mathbf{r}')$.

Electronegativity (χ) may be obtained as[23]

$$\chi = -\mu = \frac{Z}{r_C} - \int \frac{\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}_C|}\,\mathrm{d}\mathbf{r} \qquad (11)$$

where r_C defines a point (a measure[23] of the covalent radius of an atom) where the total electrostatic potential is equal to the chemical potential (originally prescribed by Gordy[24]) as the sum of functional derivatives of kinetic and exchange correlation energies with respect to $\rho(\mathbf{r})$ is zero at that point, vide the Euler−Lagrange equation,

$$\frac{\delta E[\rho]}{\delta\rho(\mathbf{r})} = \mu \qquad (12)$$

In the present work, we compare the two different approaches for calculating the reactivity parameters and also see the effect of two different ways of incorporating the effect of confinement. Section 2 presents the numerical details, and Section 3 discusses the results obtained. Finally, Section 4 contains some concluding remarks.

2. Numerical Details

Numerical solution is launched with the solution of the nonrelativistic Hartree−Fock−Slater equation for atoms and ions within the standard Herman−Skillman code.[25] This provides the self-consistent field (SCF) wave functions. The effect of confinement and subsequently that of high pressure on an atom/ion is simulated in two different ways: (A) In the first

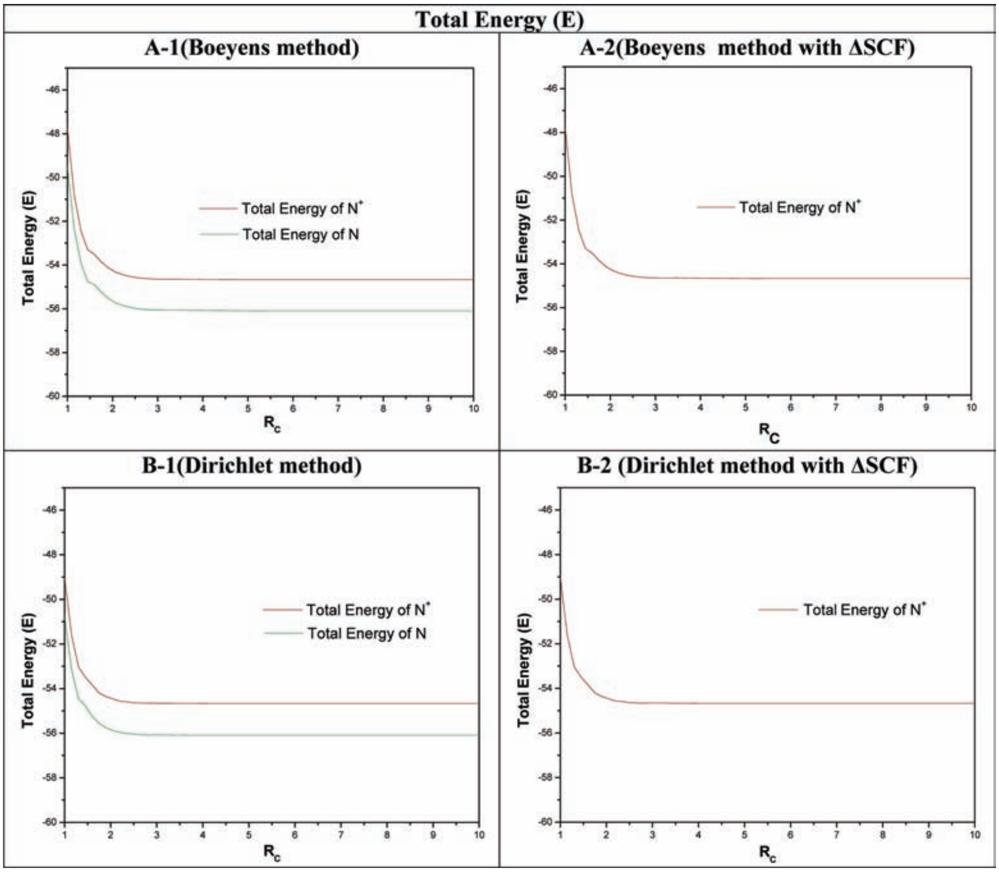

Figure 1. Plots of total energy (E, au) versus cutoff radius (R_C, au) for N (green —) and N^+ (wine —) confined in a spherical box.

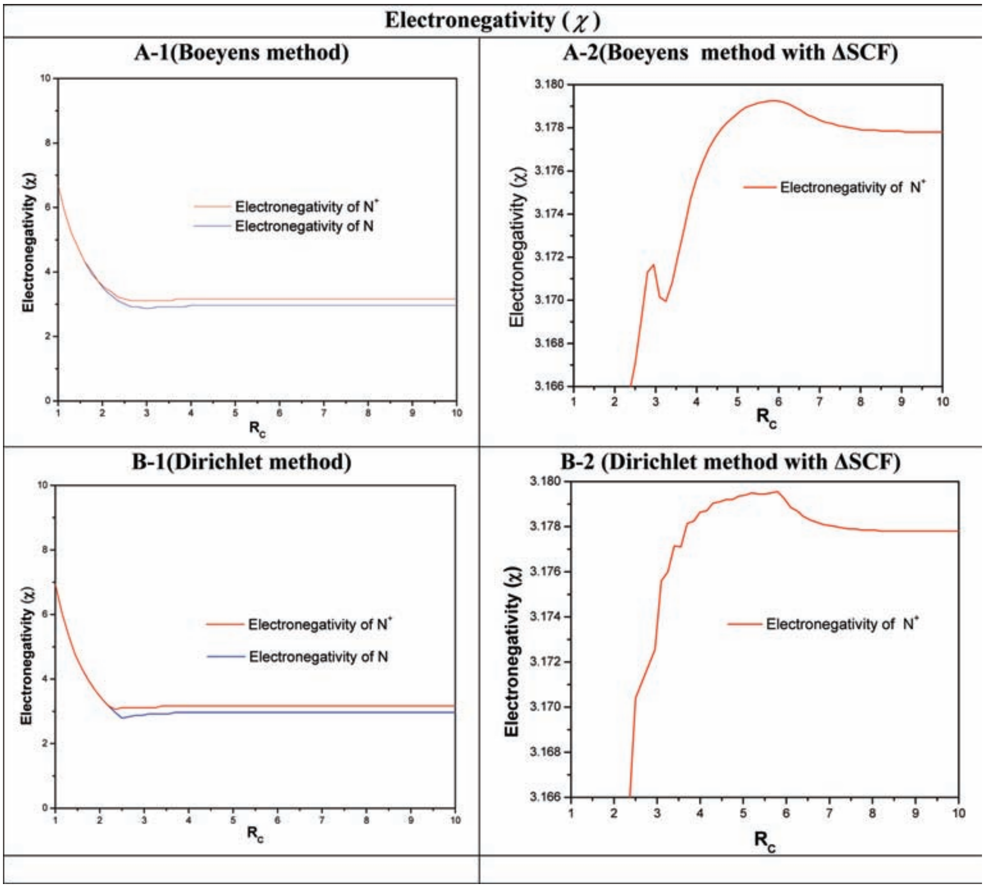

Figure 2. Plots of electronegativity (χ, au) versus cutoff radius (R_C, au) for N (blue —) and N$^+$ (red —) confined in a spherical box.

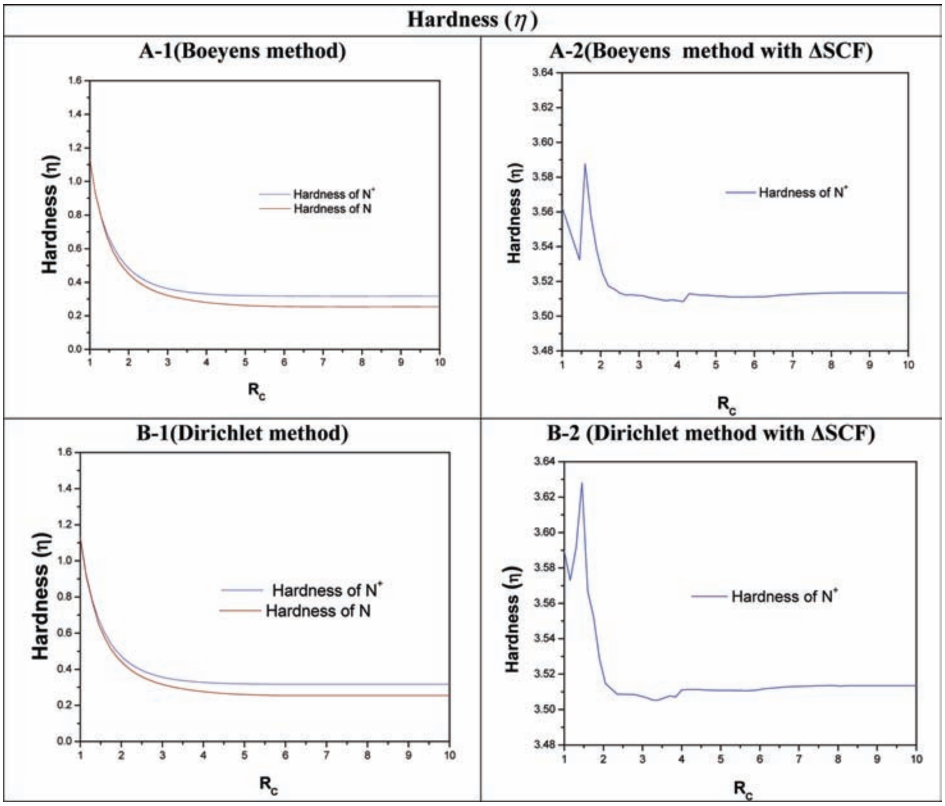

Figure 3. Plots of hardness (η, au) versus cutoff radius (R_C, au.) for N (wine —) and N$^+$ (blue —) confined in a spherical box.

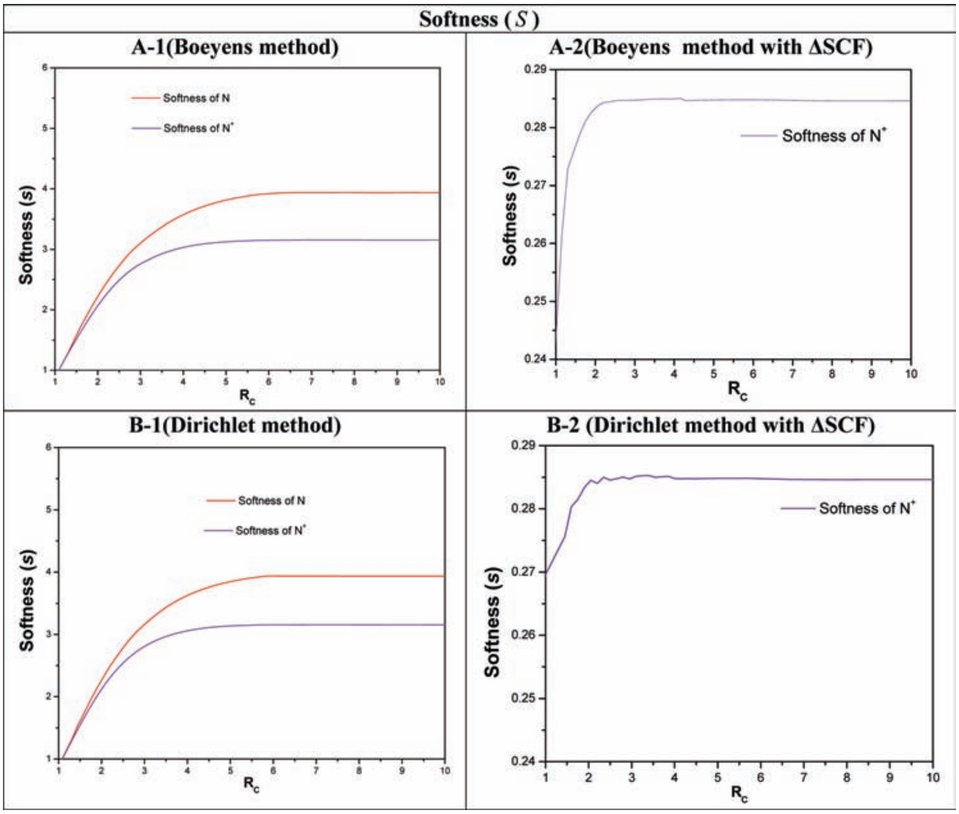

Figure 4. Plots of softness (S, au) versus cutoff radius (R_C, au) for N (red —) and N^+ (violet —) confined in a spherical box.

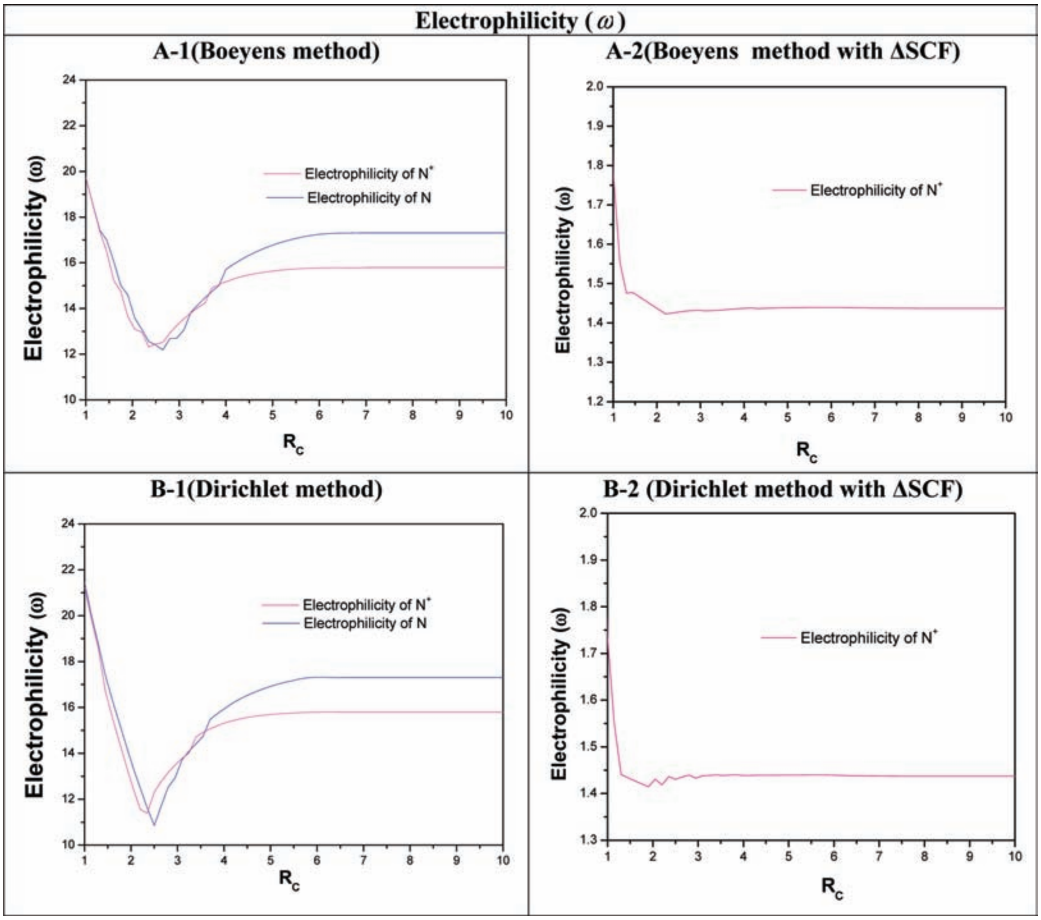

Figure 5. Plots of electrophilicity (ω, au) versus cutoff radius (R_C, au) for N (blue —) and N^+ (magenta —) confined in a spherical box.

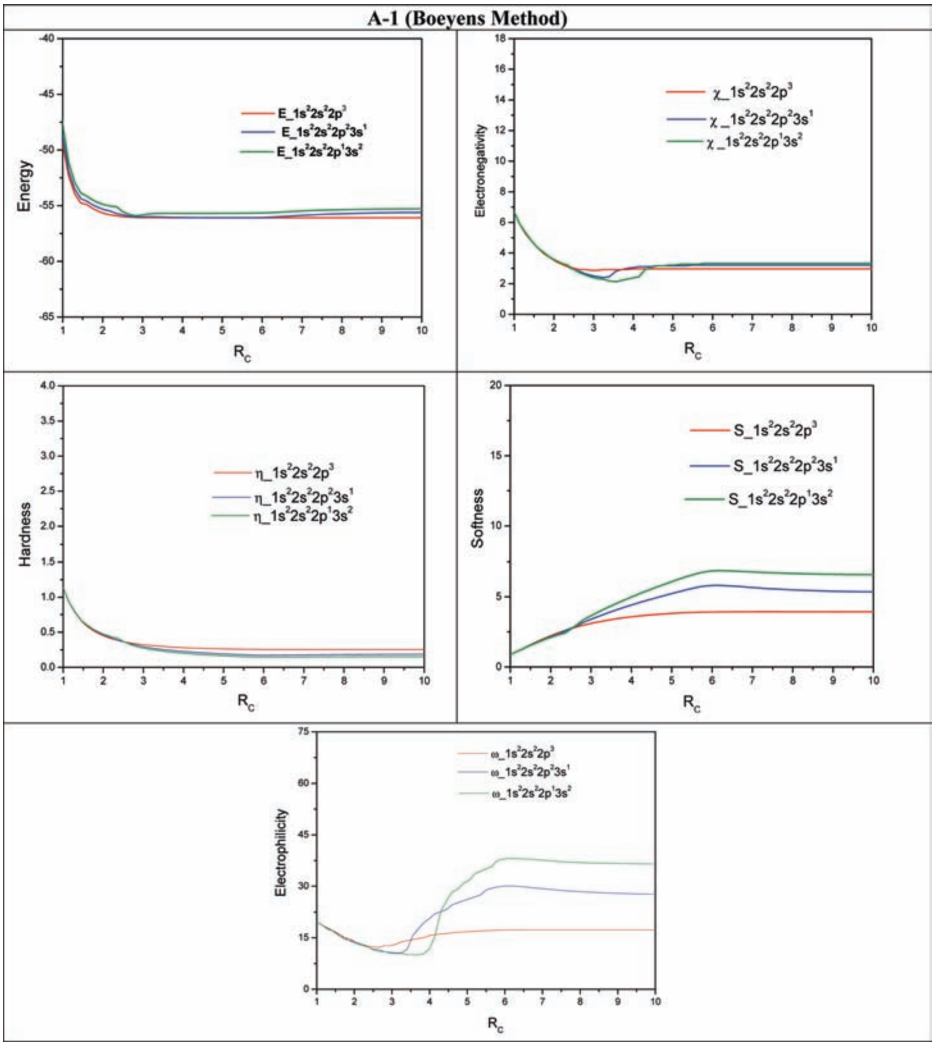

Figure 6. Plots of total energy (E), electronegativity (χ), hardness (η), softness (S), and electrophilicity (ω, au) versus cutoff radius (R_C, au) for the N atom confined in a spherical box using the Boeyens cutoff function method.

method, the SCF wave function is multiplied by a step function of the form $\Theta = \exp[(-r/R_C)^\lambda]$, as suggested by Boeyens.[26] Here R_C is the cutoff radius of the spherical box on whose surface the wave function vanishes,[26] and λ is a parameter whose value is taken to be 20, as suggested by Boeyens.[26] In this method, the step function (cutoff function) is used before normalization and during each iteration cycle. (B) In the second method, the confinement is incorporated by using an appropriate Dirichlet boundary condition so that the wave function goes to zero at the cutoff radius, R_C. Because the boundary condition is a part of the variational optimization, method B is definitely superior to the method A. Once we obtain the wave function or density by solving the Herman−Skillman program modified as in A and B, reactivity parameters are calculated. We would like to emphasize that the main aim of the present work is not to provide exact numbers but to check and to compare the qualitative trends vis-à-vis to highlight the importance of the Dirichlet boundary condition (method B) versus that of the cutoff function method of Boeyens (method A). We compare the following quantities: the energy (E), electronegativity (χ), hardness (η), softness (S), and electrophilicity (ω). The energy is calculated by incorporating the self-consistent Hartree−Fock−Slater density in eq 6 in all four cases. The Hartree−Fock−Slater energy is not used because we would like to check the effect of different boundary conditions vis-à-vis different ways of calculating reactivity parameters. The effect of varying the energy functionals (already done in refs 1−4 taken together) may be tried as a separate research problem altogether. Two different approaches have been adopted in calculating the reactivity parameters: (1) Electronegativity (χ) is calculated using the Gordy's prescription (eq 11), and hardness (η) is calculated as a density functional (eq 9) wherein the $f(\mathbf{r})$ is calculated using the Fuentealba's prescription[22] and they are used to calculate the other parameters. (2) Electronegativity (χ) and hardness (η) are, respectively, calculated using eqs 4 and 5, where I and A are obtained through the standard ΔSCF method using the energies of the M- and ($M \pm 1$)-electron species. It may be noted that whereas refs 1 and 2 correspond to an A-1-type technique, refs 3 and 4 correspond to a B-2-type technique. In the present work, we obtain the parameters from an A-2- and a B-1-type techniques as well. Because the qualitative trends do not vary much[1,2] in atoms and their cations and it is not straightforward to calculate anions or unoccupied molecular orbitals in a Herman−Skilman program for approach 2, we restrict only to a cation. For the approach 1, we calculate both the atom and its cation. We consider nitrogen to be a representative test case. To be precise, we adopt four numerical techniques as follows:

A-1 Technique. Boeyens cutoff function method. Reactivity parameters are calculated using eqs 9 and 11.

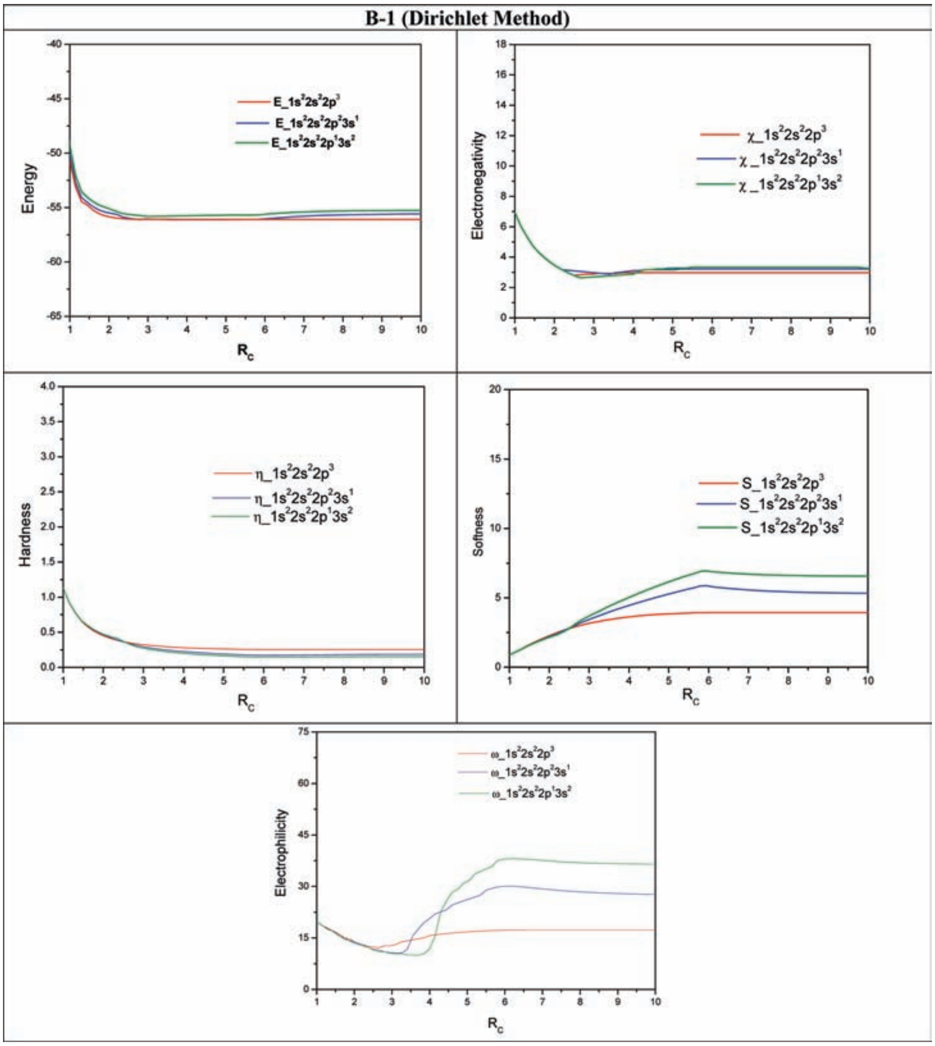

Figure 7. Plots of total energy (E), electronegativity (χ), hardness (η), softness (S), and electrophilicity (ω, au) versus cutoff radius (R_C, au) for the N atom confined in a spherical box using the Dirichlet boundary condition method.

A-2 Technique. Boeyens cutoff function method. Reactivity parameters are calculated using eqs 4 and 5 augmented by a standard ΔSCF procedure.

B-1 Technique. Dirichlet boundary condition method. Reactivity parameters are calculated using eqs 9 and 11.

B-2 Technique. Dirichlet boundary condition method. Reactivity parameters are calculated using eqs 4 and 5 augmented by a standard Δ*S*CF procedure.

To check whether other electronic configurations correspond to the ground state in a confined situation, we try various configurations and use them to generate the reactivity parameters. For the N atom, we solve the Hartree−Fock−Slater equation self-consistently for the $1s^22s^22p^3$, $1s^22s^22p^23s^1$, and $1s^22s^22p^13s^2$ configurations. In a different set for the N^+ ion, we start with (a) $1s^22s^22p^2$ and (b) $1s^22s^22p^13s^1$ configurations so that the associated ($M + 1$)-electron species (N atom) corresponds to (c) $1s^22s^22p^3$, (d) $1s^22s^22p^23s^1$, and (e) $1s^22s^22p^13s^2$ configurations and the ($M - 1$)-electron species (N^{2+} ion) corresponds to (f) $1s^22s^22p^1$ and (g) $1s^22s^23s^1$ configurations. Now the application of the ΔSCF technique on M- and $M \pm 1$- electron systems for calculating I and A values may be envisaged in six different ways: (i) f a c, (ii) f a d, (iii) f b d, (iv) f b e, (v) g b d, and (vi) g b e. We generate I and A and then all of the reactivity parameters for all six combinations.

3. Results and Discussion

Figures 1−5, respectively, present the total energy (E), electronegativity (χ), hardness (η), softness (S), and electrophilicity (ω). Each Figure comprises four panels pertaining to the four methods adopted here: A-1, A-2, B-1, and B-2. In all Figures, A-1 reproduces the trends as presented in refs 1 and 2, whereas the same trends as those presented in refs 3 and 4 are reproduced (at least qualitatively) in B-2. An analysis of the overall qualitative trends obtained in B-1 and A-2 vis-à-vis those obtained in A-1 and B-2 delineates that it is the approaches 1 and 2 rather than the methods A and B that bring in discernible qualitative changes. An $F[\rho(\mathbf{r})]$ with proper first- and second-order functional derivatives and a good quality $f(\mathbf{r})$ may diminish the difference between the quantitative values of a given reactivity index using approaches 1 and 2, respectively, at least for the very large cutoff radii.

In Figure 1, the energy increases abruptly in A-1 and B-1 as the cutoff radius decreases; however, it does not increase as much in A-2 and B-2 as was reported in refs 3 and 4.

Although electronegativity increases abruptly (Figure 2) for small R_C values in A-1 and B-1, it decreases for small R_C values in A-2 and B-2, as was reported in ref 3. It may be mentioned that the χ behaviors in A-2 and B-2 are different because of different methods used. However, the change in the gross

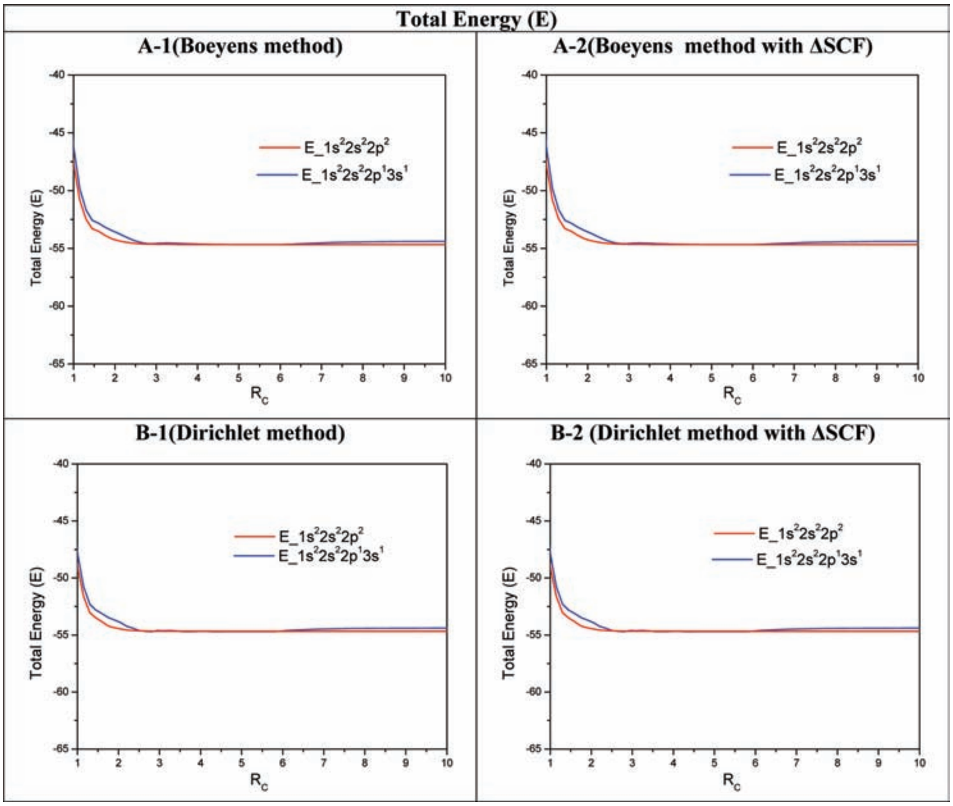

Figure 8. Plots of total energy (*E*, au) versus cutoff radius (R_C, au) for two different electronic configurations of N^+ ion (red — ($1s^22s^22p^2$) and blue — ($1s^22s^22p^13s^1$)) confined in a spherical box.

behavior in going from approach 1 (χ increases at small R_C) to approach 2 (χ decreases at small R_C) is easily discernible (cf. ref 3).

Figure 3 depicts the effect of confinement on hardness, which increases as R_C decreases in A-1 and B-1 but shows a further decrease (cf. refs 3 and 4), followed by a nominal increase, in A-2 and B-2. In particular, the B-2 curve shows a striking similarity in the qualitative η behavior with that presented in Figure 5 of ref 3. Because the results are completely numerical, it is difficult to analyze the reasons for the differences in qualitative trends in the four methods. It is even premature to claim that these results can be generalized to other atomic and molecular systems. In ref 4a, Borgoo et al. have highlighted qualitatively different hardness trends on confinement, for different atoms (He, Ne, Mg) and also for different molecules (ethylene, toluene, benzene, naphthalene). Even they have mentioned different qualitative trends in the hardness behavior for different numerical techniques used, as in the present study.

Softness (Figure 4) and electrophilicity (Figure 5) also reproduce reported qualitative trends if the ΔSCF technique is used. Softness decreases and electrophilicity increases as R_C tends to zero, and both of them attain relatively small values. Figures 6 and 7, respectively, present A-1 and B-1 results for the N atom in three different electronic configurations, viz., $1s^22s^22p^3$, $1s^22s^22p^23s^1$, and $1s^22s^22p^13s^2$. In a very small region, we notice a crossover in the energy plot. Qualitative trends in the χ and η behavior do not change much for different configurations, which is a bit more conspicuous in the *S* and ω plots. Further work is in progress.

In a very recent article[27] from a completely different perspective within a time-dependent DFT framework, it has been shown that some of the Figures from refs 1 and 2 do appear in these calculations as well, apart from some other Hartree−Fock calculations mentioned in this paper.

Variation in energy with the cutoff radius of the N^+ ion for two different electronic configurations, viz., $1s^22s^22p^2$ and $1s^22s^22p^13s^1$, in all four methods, that is, A-1, A-2, B-1, and B-2, is depicted in Figure 8. Related variations in χ, η, *S*, and ω with the cutoff radius are presented in Figures S1−S4, respectively (Supporting Information). The *I* and *A* values for the A-2 and B-2 techniques are calculated in six different ways as described above. On average, the qualitative trends do not change much, except for the η, *S*, and ω plots in a couple of cases, for example, f b d and f b e, presumably because of the addition of a new 3s orbital in the f b combination.

4. Concluding Remarks

The effect of spherical confinement on the reactivity of atoms and ions is reported wherein two different ways of incorporating the pressure effects and two approaches in calculating the reactivity parameters are used. No drastic change in qualitative trends is observed for different electronic states in most cases. Although the proper Dirichlet condition should be used in these calculations, previously reported discrepancies in the results are more due to the difference in the formulas used for the calculation of the reactivity parameters than to the use of the Dirichlet condition over the cutoff function method.

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Supporting Information Available: Plots of electronegativity, hardness, softness, and electrophilicity versus cutoff radius. This material is available free of charge via the Internet at http://pubs.acs.org.

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