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REGULAR ARTICLE

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Electrostatic exchange-correlation charge density in Be and Ne: quantal density functional theoretic analysis

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Abstract Using classical electrostatics, the total effective integrated charge-density function is calculated for Be and Ne using the multiplicative potentials derived from (1) Hartree and (2) Hartree–Fock approximation to quantal density functional theory (3)exchange-only optimized effective potential and (4) Kohn–Sham exchange-correlation potential using the quantum Monte Carlo density. The evolution of effective integrated charge-density function for these atoms is examined as the electron correlation is built up stepwise from its absence to the stage of its near complete presence. These results provide a deeper understanding of the Kohn–Sham exchange-correlation potential in terms the correspondingly defined integrated charge-density functions based on the Poisson equation.

1 Introduction

Development of accurate multiplicative potentials with computational simplicity continues to be a major research area of interest in chemistry, physics, and biology. Presently, the most popular among them is the Kohn–Sham (KS) model of *non-interacting* electrons [1], which presents an implementation of the Hohenberg-Kohn theorems [2] of density functional theory (DFT). The KS-spin orbitals, $\{\phi_i^\sigma\}$, are introduced to construct the ground state density, $\rho(\mathrm{r})$, of atoms and molecules. In particular,

$$\rho(\mathbf{r}) = \sum_{\sigma=\alpha,\beta} \sum_{i=1}^{N_\sigma} \left|\phi_i^\sigma(r)\right|^2, \tag{1}$$

where σ denotes the spin of the i-th state and the first sum runs over all occupied states and the total density $\rho = \rho^\alpha + \rho^\beta$, the sum of individual spin densities. The total energy is expressed as

$$E = \sum_{\sigma=\alpha,\beta} \sum_{i=1}^{N_\sigma} \langle \phi_i^\sigma | -\tfrac{1}{2}\nabla^2 | \phi_i^\sigma \rangle + \int \mathrm{d}\mathbf{r}\, \rho(\mathbf{r})\, \upsilon(\mathbf{r}) + \frac{1}{2} \iint \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{\mathrm{xc}}[\rho]. \tag{2}$$

In Eq. (2), the terms on the right denote the non-interacting kinetic energy, external potential, Hartree energy component of the electron–electron interaction, and the central quantity of the KS-model —the exchange-correlation functional, E_{xc}, respectively. The correlation-kinetic energy, τ_c, is the excess in the true total kinetic energy over the kinetic energy of the non-interacting model system included in E_{xc}. The variationally determined KS-spin orbitals can be obtained as the solutions of the KS-equations,

$$\left(-\tfrac{1}{2}\nabla^2 + \upsilon_{\mathrm{eff}}^\sigma(\mathbf{r})\right) \phi_i^\sigma(\mathbf{r}) = \varepsilon_i^\sigma\, \phi_i^\sigma(\mathbf{r}), \tag{3}$$

with

$$\begin{aligned}\upsilon_{\mathrm{eff}}^\sigma(\mathbf{r}) &= \upsilon(\mathbf{r}) + \int \mathrm{d}\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \upsilon_{\mathrm{xc}}^\sigma(\mathbf{r}) \\ &= \upsilon_{\mathrm{eff}}^\rho(\mathbf{r}) = \nu(\mathbf{r}) + \upsilon_{ee}^\sigma(\mathbf{r}),\end{aligned} \tag{4}$$

where the external potential $\upsilon(\mathbf{r})$ for a free atom with nuclear charge Z is given by −Z/r. The effective KS potential electronic potential, $\upsilon_{ee}^\sigma(\mathbf{r})$, is interpreted as resulting from the electron correlation effects due to the Pauli exclusion principle, Coulomb repulsion, and as noted above a correlation-kinetic contribution, respectively. In this paper, we have used the sensitive parameter of the electrostatic-integrated exchange-correlation charge density for Be and Ne atoms derived from the multiplicative potentials constructed in four different stages (a) Hartree approximation of the quantal density functional, Q-DFT, theory [3,4] in which all correlation effects are suppressed (b) Hartree-Fock (HF) approximation of Q-DFT [3–6] wherein only the Pauli correlation

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This paper is dedicated to Professor Karl Jug on the occasion of his 65th Birthday

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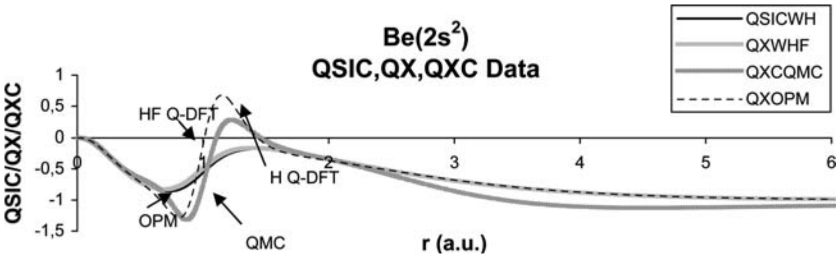

Fig. 1 The plot of $Q_{\mathrm{SIC}}^{Wh}(r)$, $Q_x^{Wx}(r)$,$Q_x^{\mathrm{OPM}}(r)$ and $Q_{\mathrm{xc}}^{\mathrm{QMC}}(r)$ as a function of r for Be(2s^2). The quantities $Q_{\mathrm{SIC}}^{Wh}(r)$, $Q_x^{Wx}(r)$, $Q_x^{\mathrm{OPM}}(r)$ and $Q_{\mathrm{xc}}^{\mathrm{QMC}}(r)$, respectively, include no correlation, exchange-only, exchange-only with first-order correlation-kinetic, and exchange-correlation with full correlation-kinetic effects in the multiplicative effective potential

effects are included (c) the exchange- only optimized potential model, (OPM) [7–10], which includes the Pauli correlation along with the first-order correlation kinetic effects [11] and finally (d) the quantum Monte Carlo density based [12, 13] KS exchange-correlation potential. In Sect. 2, we present a brief outline of the Q-DFT to illustrate the construction of potentials (a)–(b). In Sect. 3, we give a short account of the recently introduced concept of the electrostatic integrated exchange charge density. The results and conclusions of our work are presented in Sect. 3. The purpose of this work is to study the effects of the step-wise building up of the electron–electron interaction into the effective multiplicative potential on the electron density for Be and Ne. To our knowledge, this letter reports the first calculations using a carefully selected set of local(multiplicative) potential for analyzing the potential-density relationship in atoms.

2 Quantal density functional theory approach to v_{ee} (r)

In this section, a brief outline of the *quantal* density functional theory [3–6], Q-DFT, will be presented. For a detailed description of the Q-DFT, we refer to the available publications in the literature [3–6, 11, 15]. Within the Q-DFT, the total exchange-correlation potential, $v_{ee}\,(\mathbf{r})$, is calculated following the Coulomb law as work done in moving an electron from infinity to the reference location against the total conservative field, $\mathbf{F}(\mathbf{r})$:

$$v_{ee}\,(\mathbf{r}) = \frac{\delta E_{ee}^{KS}\,[\rho]}{\delta\rho\,(r)} = -\int\limits_{\infty}^{r} \mathbf{F}(\mathbf{r}')\mathrm{d}\ell'. \tag{5}$$

The total field is always conservative and is given as the sum:

$$\mathbf{F}(\mathbf{r}) = \mathbf{E}_{ee}(\mathbf{r}) + \mathbf{Z}_{t_c}(\mathbf{r}), \tag{6}$$

where the field $\mathbf{E}_{ee}\,(\mathbf{r})$ arising from the pair-correlation density g$(\mathbf{r}, \mathbf{r}')$ as the *quantal* source charge and representing the Pauli and Coulomb correlation effects is

$$\mathbf{E}_{ee}(\mathbf{r}) = \int \frac{g(\mathbf{r}, \mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3}\mathrm{d}\mathbf{r}'. \tag{7}$$

The correlation-kinetic field $\mathbf{Z}_{t_c}\,(\mathbf{r})$ arises from the kinetic-energy-density tensor [11, 15], $t_{\alpha\beta}\,(\mathbf{r})$. It is the difference of the fields derived from the tensor for the interacting and Kohn-Sham non-interacting systems. The gradient of the potential, $\nabla v_{ee}\,(\mathbf{r}) = -\mathbf{F}(\mathbf{r})$, is related to the conservative field through the rigorous relationship given by $v_{ee}\,(\mathbf{r})$ under the condition of path independence of the total work done, which implies that $\nabla \times \mathbf{F}(\mathbf{r}) = \mathbf{0}$. We note here that whereas the sum of the total work done against $\mathbf{F}(\mathbf{r})$ is always path-independent, individual components of the work done [see, e.g. Eq. (8) below] are not so in general. The individual components are path-independent for the special cases of spherically symmetric systems such as the closed-shell atoms considered in this work wherein $\nabla \times \mathbf{E}_{ee}(\mathbf{r}) = \nabla \times \mathbf{Z}_{t_c}(\mathbf{r}) = \mathbf{0}$.

The potential $v_{\mathrm{ee}}\,(\mathbf{r})$ can be calculated as the sum of the corresponding work done according to

$$v_{ee}(\mathbf{r}) = W_{ee}(\mathbf{r}) + W_{t_c}(\mathbf{r}), \tag{8}$$

where,

$$W_{ee}(\mathbf{r}) = -\int\limits_{\infty}^{r} \mathbf{E}_{ee_t}\left(\mathbf{r}'\right)\mathrm{d}\mathbf{l}' \tag{9}$$

$$W_{t_c}(\mathbf{r}) = -\int\limits_{\infty}^{r} \mathbf{Z}_{t_c}\left(\mathbf{r}'\right)\mathrm{d}\mathbf{l}'. \tag{10}$$

The Hartree and HF electron densities are exactly reproduced by their analogous Q-DFT representations within which a correlation-kinetic component is included. In the present calculations, we have employed an approximation to the Q-DFT Hartree and QDFT Hartree–Fock procedure such that the correlation-kinetic effects are ignored completely [16]. On the other hand, the exchange-only OPM calculations are used as reference exchange-only KS model, which displays the leading correlation-kinetic effects.

Let the static self-interaction-correction (SIC) charge $q_i = \sum_\sigma \phi_i^\sigma\,(\mathbf{r})\,\phi_i^\sigma\,(\mathbf{r})$ define the SIC correction to the density as $\rho_{\mathrm{SIC}}^{\mathrm{H}}(\mathbf{r}, \mathbf{r}') = -\sum_i q_i(\mathbf{r})q_i(\mathbf{r}')/\rho\,(\mathbf{r})$ with the sum-rule

$$\int \rho_{\mathrm{SIC}}^{\mathrm{H}}(\mathbf{r}, \mathbf{r}')\mathrm{d}\mathbf{r}' = -1. \tag{11}$$

In the Hartree Q-DFT approximation, the Hartree pair-correlation density $g^{\mathrm{H}}\left(\mathbf{r}, \mathbf{r}'\right)$ is used as the quantal source charge, which is defined as $g^{\mathrm{H}}\left(\mathbf{r}, \mathbf{r}'\right) = \rho(\mathbf{r}) + \rho_{\mathrm{SIC}}^{\mathrm{H}}(\mathbf{r}, \mathbf{r}')$.

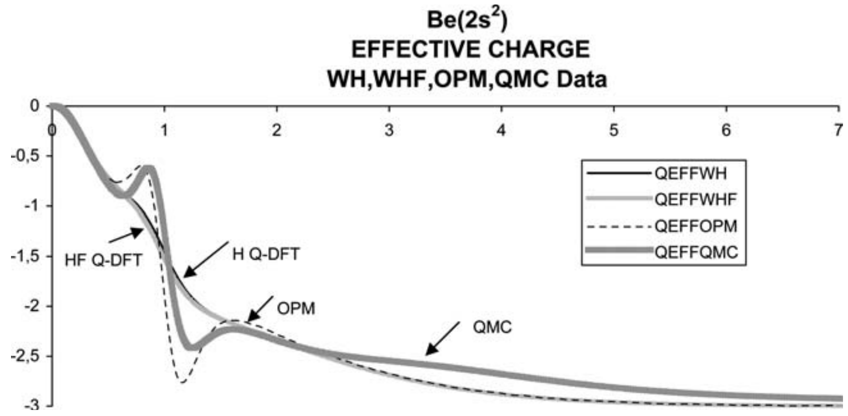

Fig. 2 The plots of total effective charge $Q_{\mathrm{eff}}(r)$ given by $Q_{\mathrm{xc}}(r) + Q_{\mathrm{h}}(r)$ corresponding to the $Q_{\mathrm{xc}}(r)$ given by $Q_{\mathrm{SIC}}^{Wh}(r)$, $Q_x^{Wx}(r)$, $Q_x^{\mathrm{OPM}}(r)$, and $Q_{\mathrm{xc}}^{\mathrm{QMC}}(r)$, respectively for Be(2s^2)

The effective potential, $v_{ee}^{\mathrm{H}}(\mathbf{r})$, is given by $W_{\mathrm{H}}(\mathbf{r}) + W_{\mathrm{SIC}}(\mathbf{r})$ with

$$W_{\mathrm{H}}(\mathbf{r}) = -\int_{\infty}^{r} \mathbf{E}_{\mathrm{H}}\left(\mathbf{r}'\right) \mathrm{d}\mathbf{l}'$$

$$= -\nabla W_{\mathrm{H}}(\mathbf{r}) = \int \mathrm{d}\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \qquad (12)$$

$$W_{\mathrm{SIC}}(\mathbf{r}) = -\int_{\infty}^{r} \mathbf{E}_{\mathrm{H}}^{\mathrm{SIC}}\left(\mathbf{r}'\right) \mathrm{d}\mathbf{l}', \qquad (13)$$

$$\mathbf{E}_{\mathrm{H}}^{\mathrm{SIC}}(\mathbf{r}) = \int \frac{\rho_{\mathrm{SIC}}^{\mathrm{H}}(\mathbf{r},\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} \mathrm{d}\mathbf{r}' \qquad (14)$$

In the HF Q-DFT approximation [3], the pair-correlation density is given by $g^{\mathrm{HF}}\left(\mathbf{r},\mathbf{r}'\right) = \rho(\mathbf{r}) + \rho_x^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')$, where $\rho_x^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')$ is the Fermi hole charge defined in the HF theory. In particular, $\rho_x^{\mathrm{HF}}(\mathbf{r},\mathbf{r}') = -\left|\gamma^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')\right|^2 / 2\rho(\mathbf{r})$, where $\gamma^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')$ denotes the HF spinless idempotent Dirac density matrix. The corresponding field due to this quantal source charge is defined as

$$\mathbf{E}_{ee}^{\mathrm{HF}}(\mathbf{r}) = \int \frac{g^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} \mathrm{d}\mathbf{r}'. \qquad (15)$$

The exchange potential in the HF Q-DFT approximation is calculated as the work done

$$W_{ee}^{\mathrm{HF}}(\mathbf{r}) = -\int_{\infty}^{r} \mathbf{E}_{ee}^{\mathrm{HF}}\left(\mathbf{r}'\right) \mathrm{d}\mathbf{l}'. \qquad (16)$$

The Fermi hole satisfies the sum rule

$$\int \rho_x^{\mathrm{HF}}(\mathbf{r},\mathbf{r}') = -1. \qquad (17)$$

We note here that Eqs. (11) (17) determine the asymptotic limit as r→ ∞ for the electrostatic exchange-correlation charge defined via the Poisson equation in Sect. 3.

3 Electrostatic exchange-correlation charge-density function $Q_{\mathrm{xc}}(\mathbf{r})$

In this section, the definition of the total integrated exchange-correlation charge and its analogues corresponding to the various multiplicative potentials considered in the present work will be given following the earlier work of Liu et al. [17], Görling [18], and March [19]. The classical electrostatic potential, $v_{\mathrm{es}}(r)$, is well known to be related to the static total charge density $\rho(\mathbf{r})$ through the Poisson equation,

$$\nabla^2 v_{es}(\mathbf{r}) = -4\pi\rho(r), \qquad (18)$$

where the total integrated charge density, $Q_h(r)$, for the spherically averaged densities is

$$Q_h(r) = -r^2 \frac{\partial v_{es}}{\partial r} = 4\pi \int_0^r \rho(r) r^2 \mathrm{d}r. \qquad (19)$$

Recently, Liu et al. [17] and Görling [18] have introduced the concept of local effective *static* exchange-correlation charge, $q_{xc}(\mathbf{r})$, using the Poisson equation,

$$\nabla^2 v_{\mathrm{xc}}(\mathbf{r}) = -4\pi q_{\mathrm{xc}}, \qquad (20)$$

where $v_{\mathrm{xc}}(\mathbf{r})$ represents the *total* exchange-correlation potential. March [19] has discussed, independently, using the Poisson equation, the associated *total* integrated radial static exchange-correlation charge density for the spherical atoms,

$$Q_{\mathrm{xc}}(r) = 4\pi \int_0^r q_{xc}(r) r^2 \mathrm{d}r. \qquad (21)$$

Liu et al. [17] have reported the calculations of $q_{\mathrm{xc}}(r)$ for He, Ne, and Ar atoms. Menconi et al. [20] have reported similar studies on closed-shell systems He, Ne, HF, CO, and N$_2$, using the effective KS potential derived from accurate input densities. Very recently, it has been shown [21] that $Q_{\mathrm{xc}}(r)$ accurately displays the shell boundaries in closed-shell atoms and provides a deeper understanding of the stability of the closed-shell negative ions.

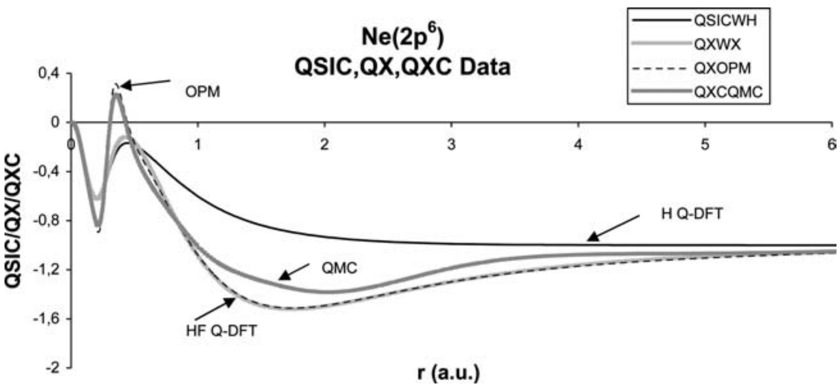

Fig. 3 The plot of $Q^{Wh}_{\mathrm{SIC}}(r)$, $Q^{Wx}_{x}(r)$, $Q^{\mathrm{OPM}}_{x}(r)$, and $Q^{\mathrm{QMC}}_{\mathrm{xc}}(r)$ as a function of r for Ne($2s^2$). The quantities $Q^{Wh}_{\mathrm{SIC}}(r)$, $Q^{Wx}_{x}(r)$, $Q^{\mathrm{OPM}}_{x}(r)$, and $Q^{\mathrm{QMC}}_{\mathrm{xc}}(r)$, respectively, include no correlation, exchange-only, exchange-only with first-order correlation-kinetic, and exchange-correlation with full correlation-kinetic effects in the multiplicative effective potential

It has been pointed out [17–19] that $Q_{\mathrm{xc}}(r)$ obeys [22] interesting sum rules e.g. $|Q_{\mathrm{xc}}(r)| \to 1$, as $r \to \infty$, and $|Q_{\mathrm{xc}}(r)| \to 0$ as $r \to 0$. In addition, the quantity represented by the sum $Q_{\mathrm{xc}}(r) + Q_h(r)$ can be prescribed an interesting interpretation– it is the total effective integrated charge density, $Q_{\mathrm{eff}}(r)$, at r which the reference electrons feel in the KS-self-consistent field. The analogue of $Q_{\mathrm{xc}}(r)$ computed using the H Q-DFT, HF Q-DFT, and OPM potentials will be denoted by $Q^{Wh}_{\mathrm{SIC}}(r)$, $Q^{Wx}_{x}(r)$, and $Q^{\mathrm{OPM}}_{x}(r)$, respectively. The corresponding quantity derived from the QMC density will be represented by $Q^{\mathrm{QMC}}_{\mathrm{xc}}(r)$.

4 Results and conclusions

Approximate Q-DFT calculations have been carried out using the work potential code described and used earlier [23,24]. The exchange-only OPM calculations were performed using the code developed by Engel and Dreizler [25]. The calculations of $Q_{\mathrm{xc}}(r)$ are derived from the KS potential reported by Umrigar et al. [12,13].

In Fig. 1 we have plotted $Q^{Wh}_{\mathrm{SIC}}(r)$, $Q^{Wx}_{x}(r)$, $Q^{\mathrm{OPM}}_{x}(r)$, and $Q^{\mathrm{QMC}}_{\mathrm{xc}}(r)$, respectively, for Be atom. As compared to $Q^{Wh}_{\mathrm{SIC}}(r)$ wherein no correlation effect is included, the exchange effects lead to more compact distribution in $Q^{Wx}_{x}(r)$ with the slight shifting of the curves towards less negative values in the intermediate region defined by $1 < r < 2.5$ a.u. At large r, the two curves are almost identical. With reference to the $Q^{Wx}_{x}(r)$ estimate, the quantity $Q^{\mathrm{OPM}}_{x}(r)$ includes the first-order correlation-kinetic contribution to the integrated exchange charge density. This leads to the bumps in the inter-shell region in $Q^{\mathrm{OPM}}_{x}(r)$, with the corresponding curve becoming more compact and shifting outwards with enhanced magnitudes for its optimum values. In the inter-shell region, $Q^{\mathrm{OPM}}_{x}(r)$ characteristically attains positive values. Relative to $Q^{\mathrm{OPM}}_{x}(r)$, the function $Q^{\mathrm{QMC}}_{\mathrm{xc}}(r)$ derived from the QMC density includes contributions from the effects due to the Coulomb hole and the higher-order correlation-kinetic effects. This leads to a more compact distribution in $Q^{\mathrm{QMC}}_{\mathrm{xc}}(r)$ over the inter-shell region. At large r, $Q^{\mathrm{OPM}}_{x}(r)$ and $Q^{\mathrm{QMC}}_{\mathrm{xc}}(r)$ are found to be significantly different, indicating the importance of the Coulomb correlation and the higher-order correlation-kinetic effects in this region. Such a variation in $Q_{\mathrm{xc}}(\mathrm{r})$ gives rise to the total effective charge $Q_{\mathrm{eff}}(r)$ i.e. $Q_{\mathrm{xc}}(r) + Q_h(r)$ changing in an interesting way as the electron–electron correlation effects in the KS model are built up successively. This is displayed in Fig. 2, where the corresponding $Q_{\mathrm{eff}}(r)$ derived from the four different potentials have been plotted for Be atom. It is important to note that the more accurate OPM and QMC estimates of $Q_{\mathrm{eff}}(r)$ differ from each other as well as with the Q-DFT approximations at all r values. As noted above, a significant difference is found at large r between the QMC-derived effective charge with others highlighting the role of electron correlation effects on chemical reactivity, in general.

In Fig. 3, we have displayed $Q^{Wh}_{\mathrm{SIC}}(r)$, $Q^{Wx}_{x}(r)$, $Q^{\mathrm{OPM}}_{x}(r)$, and $Q^{\mathrm{QMC}}_{\mathrm{xc}}(r)$ for Ne atom. In contrast to the Be case where $Q^{Wh}_{\mathrm{SIC}}(r)$ and $Q^{Wx}_{x}(r)$ are found to be quite similar, the exchange contribution in HF Q-DFT potential in Ne leads to $Q^{Wx}_{x}(r)$, which is significantly different from $Q^{Wh}_{\mathrm{SIC}}(r)$, which suggests that the spatial behavior of exchange interactions is distinctly different in the s- and p-subshell electrons. Between $Q^{Wx}_{x}(r)$ and $Q^{\mathrm{OPM}}_{x}(r)$, the difference is to be attributed to the first-order correlation-kinetic effect, which shows up most prominently over the intra-shell region. The $Q^{\mathrm{QMC}}_{\mathrm{xc}}(r)$ results are found to be different over the entire region of the radial distance with its relative magnitude reduced relative to $Q^{\mathrm{OPM}}_{x}(r)$ as $r \to \infty$. The effect of the spatial variations in $Q^{Wh}_{\mathrm{SIC}}(r)$ leads to the corresponding modulations in $Q_{\mathrm{eff}}(r)$, which is displayed in Fig. 4. From Figs. 1 and 3, it is clear that the $Q^{Wx}_{x}(r)$ results closely follow the $Q^{\mathrm{QMC}}_{\mathrm{xc}}(r)$ curve over the entire range of the radial distance considered. This implies that there is a strong cancellation between the Coulomb correlation and correlation-kinetic effects.The results displayed in Figs. 1–4 establish the exchange-correlation charge-density integral defined in Eq. (21) as a very sensitive chemical reactivity parameter in terms of $Q_{\mathrm{eff}}(r)$. In addition, such data on Be and Ne corresponding to the QMC density should serve as the bench mark for testing the various approximate exchange-correlation functionals.

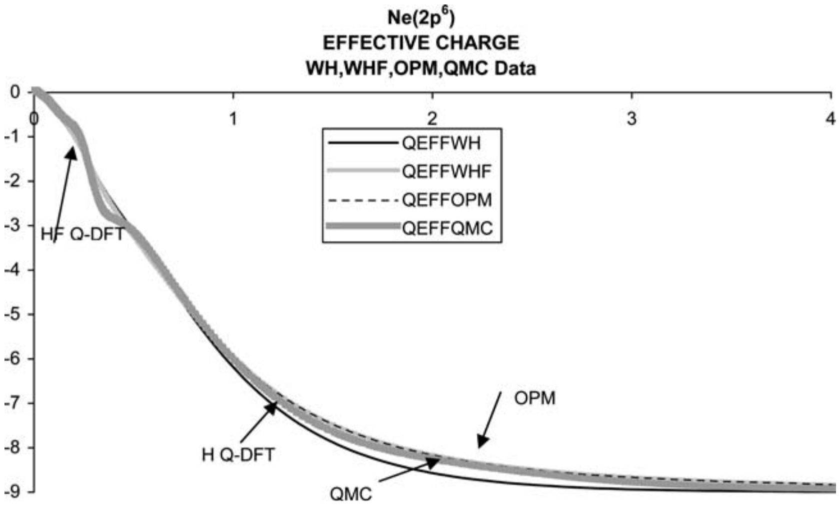

Fig. 4 The plots of total effective charge $Q_{\text{eff}}(r)$ given by $Q_{\text{xc}}(r) + Q_h(r)$ corresponding to the $Q_{\text{xc}}(r)$ given by $Q^{\text{Wh}}_{\text{SIC}}(r)$, $Q^{\text{Wx}}_x(r)$, $Q^{\text{OPM}}_x(r)$ and $Q^{\text{QMC}}_{\text{xc}}(r)$, respectively for Ne(2s^2)

There exists an interesting possibility of directly analyzing the $q_h(r)$ and $q_{\text{xc}}(r)$ effective charges and study their asymptotic behavior. Such a study would also throw light on the differences over the radial space brought about on integration in $Q_{\text{xc}}(r)$ and $Q_{\text{ceff}}(r)$ at the various levels of the treatment of electron–electron interaction. Further, the electron density derived from the four different potentials considered here can be directly used to study the information contained in it due to the different parts of the electron–electron interaction. For example, a surprisal analysis [26] using the cross-entropy with Hartree Q-DFT density as a reference would reveal the extra information in the test density due to the additional interaction in the potential used to generate the latter. Such a study would complement the studies involving the mapping [27] of exchange-correlation potential from the molecular densities. The research work involving the above topics are currently under progress.

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