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Citation: *J. Chem. Phys.* **127**, 114708 (2007); doi: 10.1063/1.2768523

View online: <http://dx.doi.org/10.1063/1.2768523>

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# Electronic structure of spherical quantum dots using coupled cluster method

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(Received 8 May 2007; accepted 11 July 2007; published online 19 September 2007)

2, 6, 12, and 20 electron quantum dots have been studied using coupled cluster at singles and doubles level and extensive multireference coupled cluster (MRCC) method. A Fock-space version of MRCC (FSMRCC) containing single hole-particle excited determinants has been used to calculate low-lying excited states of the above system. The ionization potential and electron affinity are also calculated. The effect of correlation energy on excitation energy and charge density is shown by calculating them at the high density region (low value of density parameter  $r_s$ ) and at the low density region (high value of density parameter  $r_s$ ). © 2007 American Institute of Physics.

[DOI: [10.1063/1.2768523](https://doi.org/10.1063/1.2768523)]

## I. INTRODUCTION

Quantum dots are zero dimensional electron systems which are also called artificial atoms because of the many similarities they have with the real atoms, such as discrete electronic spectra and degenerate energy levels.<sup>1-3</sup> The quantum dots are a manifestation of confined electron systems. The number of electrons and the size of such a confined electron gas are highly tunable; hence, they can be used to investigate the various properties of interacting many-body systems. A diverse variety of applications ranging from single electron transistor, lasers, diodes to quantum computing have made quantum dots an interesting object for extensive theoretical<sup>3,5</sup> and experimental investigations,<sup>1,2</sup> since their early realization in the early 1980s.<sup>4</sup> In recent years, the electronic structure of quantum dots has been studied by a variety of techniques. The majority of the work reported is with parabolic confining potential.<sup>3</sup> There have been several well established studies on quantum dots using spin density functional theory (SDFT),<sup>3,6,7</sup> The Hartree-Fock<sup>8,9</sup> (HF) and exact diagonalization<sup>10-12</sup> (ED) methods have also been used to study quantum dots. It is known that the SDFT suffers from broken symmetry problem while HF fails to describe electron correlation. Although ED is able to treat the correlations exactly, it is limited to a few electron systems (four to six electrons).

There are also many traditional methods to study excited states including ED,<sup>13,14</sup> time dependent density functional (TDDFT) theory<sup>15-18</sup> and time dependent Hartree-Fock (TDHF) theory.<sup>19,20</sup> However, ED is limited to the study of very few frequencies. The TDDFT suffers from an unknown frequency dependence and TDHF on the other hand does not contain correlation effects which are important for the description of excited states, in particular.

Therefore, it is necessary to establish a theoretical method which provides an accurate treatment of the correla-

tion energy for the ground states as well as the excited states and remains computationally tractable for even large systems. There are a number of reasons to recommend the coupled cluster singles and doubles (CCSD) model.<sup>21</sup> One of the most important reasons is that the method is size extensive, which means that it scales properly with the size of the dot (the number of electrons). The singles and doubles model is also efficient since the treatment of the electron correlation effect grows no more rapidly than the sixth power of the number of basis functions and the method is accurate enough. CCSD is also applicable to most of the problems without modification or special symmetry conditions.

The correlation energies of ground states for two and six electron quantum dots have been reported previously using CCSD at different confining strengths  $\omega$ .<sup>22</sup> The excited state quantum dots have also been studied using a highly correlated equation of motion coupled cluster (EOMCC) method<sup>23</sup> for two electron systems while varying the confinement frequency  $\omega$ .<sup>24</sup>

In the present work, the electronic structure of the ground and excited states of two-dimensional quantum dots containing 2, 6, and 12 electrons have been computed using CCSD and completely size-extensive multireference coupled cluster (MRCC) method, respectively. MRCC has been found to be a more compact method to describe both the dynamic and nondynamic electron correlations of excited states and better suited than EOMCC for having the property of complete size extensivity.<sup>25-29</sup> In the effective Hamiltonian version of the method,<sup>26</sup> the exact energies of the states are obtained by diagonalization of a suitably defined effective Hamiltonian within a prechosen model space of important configurations. There are two primary versions of the effective Hamiltonian MRCC, one state-universal type and the other valence-universal or Fock-space type. The latter, based on the concept of a common vacuum, is suitable for

excitation energy, ionization potential, and electron affinity.<sup>29</sup> It is possible to make accurate predictions about the spin densities of the above state properties using the MRCC method.<sup>30</sup>

The paper is organized as follows: In the next section, we present a brief description of the FSMRCC method, which is already covered in literature extensively. In Sec. III, details of the external potential of quantum dots and the computational methods of using FSMRCC to quantum dots is presented. Section IV presents results and discussions.

## II. THEORY

While most of the attention has been focused on the difference energies, there has been recent interest in applying coupled cluster (CC) methods to the case of static electronic properties. Broadly the CC method can be classified into two categories, one based on a single-determinant reference function, usually a Hartree-Fock function,<sup>21</sup> and the other based on a multiconfiguration model space.<sup>29</sup>

Single reference CC models have been shown to be highly successful for nondegenerate systems. It effectively includes the “dynamical” correlation that keeps the electrons apart. However, for cases where “nondynamical” correlation is important, i.e., when several configurations might be expected to make equally important contributions to the exact wave function, the model space should include several configurations to introduce such quasidegenerate effects.

We choose the numerical Hartree-Fock solution for the closed-shell  $N$ -electron ground state  $\Phi_{\text{HF}}$  as the vacuum with respect to which holes and particles are defined. The different configurations included in the model space in the FSMRCC include holes and particles, which are called active orbitals. The number of active holes and particles defines the rank of the Fock-space for the problem. In general, for a problem for which the model space consists of  $k$  active particles and  $l$  active hole, the cluster operators must be able to destroy any subset of  $k$  active particles and  $k$  active holes. In our problem in which the model space consists of one active particle and one active hole, the normal ordered wave operator is defined by

$$\Omega = \{e^{S^{(k)}}\}, \quad (1)$$

where

$$\tilde{S}^{k,l} = \sum_{n_1=0}^k \sum_{n_2=0}^l S^{(n_1, n_2)} \quad (2)$$

or

$$\tilde{S}^{(1,1)} = S^{(0,0)} + S^{(0,1)} + S^{(1,0)} + S^{(1,1)}, \quad (3)$$

where  $S^{(n_1, n_2)}$  describes exactly  $n_1$  number of active holes and  $n_2$  number of active particles. The brackets  $\{\}$  denote the normal ordering of the operators within the parentheses.

To calculate the energies for the open-shell states like  $(N-1)$  electron states,  $(N+1)$  electron states, or the excited  $N$ -electron states, we substitute the form of the wave function in the Schrödinger equation:

$$H|\Psi_i^{(k,l)}\rangle = E_i|\Psi_i^{(k,l)}\rangle. \quad (4)$$

We can postulate the existence of a valence-universal wave operator  $\Omega$  that satisfies a Fock-space Bloch equation of the form

$$H\Omega P^{(k,l)} = \Omega H_{\text{eff}} P^{(k,l)}; \quad 0 \leq k \leq l, \quad 0 \leq l \leq 1, \quad (5)$$

where  $P^{(k,l)}$  is the projection operator onto the model space defined by the linear combination of determinants having  $k$  active particles and  $l$  active holes. This equation is solved using the subsystem embedding condition developed by Mukherjee and co-workers<sup>27,31</sup> and thus the description of lower Fock-space sectors is obtained as by-product. The equation is projected to  $P$  and  $Q$  spaces of the relevant Fock-space sectors.

The Bloch equation defines the wave operator and the effective Hamiltonian. The cluster operator following Eq. (1) must contain all excitations capable of inducing transitions from all the model space  $\Phi^{(k,l)}$  (with  $k$  and  $l$  between 0 and 1) to the corresponding virtual space.

For complete space, the valence universality is compatible with the Bloch intermediate normalization given by

$$P^{(k,l)}\Omega P^{(k,l)} = P^{(k,l)}. \quad (6)$$

However, for a general case, use of incomplete model space is quite essential and for such general cases the use of Bloch intermediate normalization is incompatible with a valence universal  $\Omega$  as was first shown by Mukherjee.<sup>32</sup> Hence the  $P$ -space projection equation gets modified. A special case of incomplete model space is a space of one active particle and one active hole, which will be used in the present paper for the calculation of excited energies. Such a model space is called quasicomplete model space. For such quasicomplete model space, it has been shown that the intermediate normalization can still be used by keeping the connected form of equations.<sup>29,33</sup> Hence, although this is formally an incomplete space, the equations form the simple structure of a complete model space.

It has been shown that for excitation energies using (1,1) model space, the amplitude of  $S_1^{(1,1)}$  operator, which takes the model space to  $\Phi_{\text{HF}}$ , does not contribute. For computational simplifications, initially

$$\bar{H} \rightarrow (He^{S^{(0,0)}})_C \quad (7)$$

is formed.  $\bar{H}$  is contracted to  $S^{(0,1)}$ ,  $S^{(1,0)}$ ,  $S^{(1,1)}$ , etc., to form the connected parts of Eq. (5).

## III. COMPUTATIONAL DETAILS

The model Hamiltonian for a quantum dot with parabolic confining potential is given by

$$H(m^*, \kappa, \omega) = \frac{-1}{2m^*} \sum \nabla_i^2 + \frac{1}{2} m^* \omega^2 \sum r_i^2 + \sum_{i>j} \frac{1}{\kappa r_{ij}}. \quad (8)$$

$m^*$  and  $\kappa$  are scaled from the problem by choosing them as  $m^* = \kappa = 1$ . Hence we have

$$E(m^*, \kappa, \omega) = \frac{m^*}{\kappa^2} E(1, 1, \omega'), \quad (9)$$

where

$$\omega' = \frac{\kappa^2}{m^*} \omega. \quad (10)$$

Typical material constants for GaAs are  $m^*=0.067$  and  $\kappa=12.4$ . The units of length and energy are scaled to effective atomic units. Effective Bohr radius  $a_B^*=9.8$  nm and effective Hartree  $H_a^*=2R_y^*=12$  meV.

The confinement potential ( $\omega$ ) and density parameter ( $r_s$ ) are related to the number of electrons in the dot.<sup>34</sup>  $r_s$  corresponds to the average particle density in the dot. For the external parabolic confinement, we have

$$\omega^2 = \frac{1}{r_s^3 \sqrt{N}}. \quad (11)$$

This clearly shows how  $r_s$  and  $\omega$  are related. It means that increasing the value of  $r_s$  results in shifting towards the low density region which is highly correlated and vice versa. When the electron density is low, the Coulombic energy increases with respect to kinetic energy and consequently the correlation effect is strongly dominant. We have solved the problem in three steps. We first obtain the HF solution by using real-space grid technique. This technique initiates the self-consistency with one of the several guesses of charge density in search of energy minima, which assures the detection of the actual energy of the ground state of the system. We have applied a grid size of  $60 \times 60$  for 2-electron dots,  $120 \times 120$  for 6-electron dots,  $160 \times 160$  for 12-electron dots, and  $200 \times 200$  for 20-electron dots. In the second step we calculate the CCSD energy which is different from HF energy by the amount of correlation energy. Finally Fock-space MRCC calculates the excitation energies, ionization potential, and electron affinities. The (0,0) sector is associated with the ground state, the (0,1) sector with singly ionized states, the (1,0) sector with electron attached states, and the (1,1) sector with singly excited states. For 2-electron dot, one active hole and five active particles generate the model space

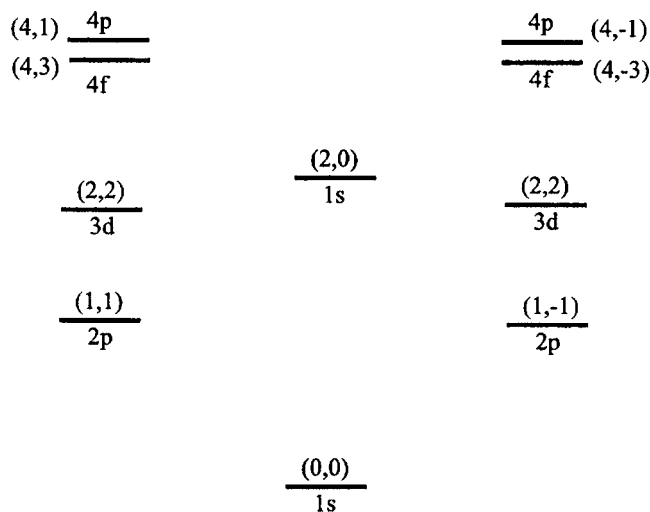


FIG. 1. The closed-shell HF orbital energy diagram.

TABLE I. The HF and CCSD energies for a  $N=2$  electron dot at different values of  $\omega=0.2, 0.4, 0.6, 0.8,$  and  $1$ . Energies are measured in effective Hartree atomic units.

$\omega$	HF energy	CCSD energy	CCSD energy (Henderson <i>et al.</i> )
0.2	0.882	0.731	...
0.4	1.508	1.366	1.377
0.6	2.082	1.932	1.939
0.8	2.631	2.475	2.479
1.0	3.161	3.001	3.003

and for 6-electron dot, three active holes and seven active particles have been chosen to establish the model space. For 12-electron dot, three active holes and four active particles are chosen as the model space.

It is possible to treat confined electrons over wide ranges of frequencies by changing the value of  $\omega$ . With GaAs material constants, frequencies of interest scale into a range more typical of atomic and molecular systems where traditional quantum chemical techniques can be applied. Here, in each case, we vary values of  $\omega$  from 0.2 to 1 effective Hartree and calculate the corresponding ground state and excitation energies (EE), ionization potential (IP), and electron affinity (EA).

## IV. RESULTS AND DISCUSSIONS

For the sake of completeness we show the single particle eigenvalue spectrum for the noninteracting case in Fig. 1. Clearly the electron counts of 2, 6, 12, and 20 are magic numbers as the corresponding systems are closed-shell ones. Because the electrons are confined by a harmonic potential rather than a Coulombic potential, the angular momentum for a principal quantum number  $n$  runs from  $n$  to 0, decreasing by steps of 2 instead of 1. On the other hand, there are only two functions of a given angular momentum and principal quantum numbers  $n$  and  $\ell$  (the radial and angular momentum quantum numbers).

We have studied the electronic structure of closed-shell quantum dots using CCSD and MRCC methods for  $N=2, 6,$  and  $12$ . We have studied the correlation energy, excitation energy, ionization potential, and electron affinity in different density regions by varying the value in each of the 2, 6, and 12 electron quantum dots.

In Table I we show the total energies obtained by HF and

TABLE II. The HF, CCSD, and correlation energies for  $N=2, 6, 12,$  and  $20$  electron quantum dots at  $\omega=1$ . Energies are measured in effective Hartree atomic units.

$N$	HF energy	CCSD energy	Correlation energy
2	3.162	3.001	0.160
6	20.719	20.229	0.489
12	66.914	65.982	0.932
20	109.081	107.670	1.411



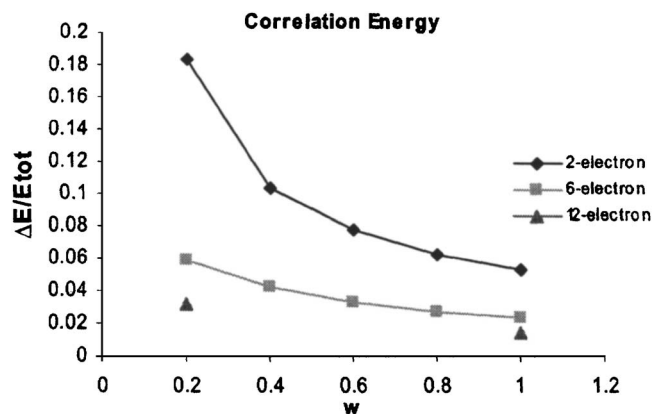


FIG. 2. Correlation energy as a fraction of total energy for  $N=2$  and 6 electron quantum dots. Correlation energies are measured in effective Hartree atomic units.

CCSD methods along with the earlier results of Henderson *et al.* for  $\omega=1$ . An excellent agreement with their results may be noted.

In Table II, we show ground state energies for  $N=2, 6, 12$ , and 20 electron dots calculated using HF and CCSD methods at  $\omega=1$ . The correlation energies are also calculated for each of the cases.

Figure 2 shows the effect of varying the value of  $\omega$  on the correlation energies for  $N=2, 6$ , and 12 electron dots. The correlation energy is plotted as a fraction of total energy. Recalling that  $\omega$  and  $r_s$  are inversely proportional, it must be noted that when  $r_s$  increases, the Coulombic energy increases, which results in increase of the correlation energy. Typically, it can be seen that for a two-electron dot the correlation energy is of the order of 18% of the total energy at  $\omega=0.2$  ( $r_s=2.6$ ). We can also see that at lower confining potential, the correlation energy becomes more important.

The effect of density ( $r_s$ ) on the energy levels can be seen in Fig. 3, where we have shown the eigenspectrum for two values of  $r_s$  ( $N=6, r_s=6.0$  and  $r_s=0.75$ ). It is clear that at high density, the energy levels are well separated. It shows the consistency of ionization potential, excitation energy, and electron affinity with varying the  $r_s$ . The  $r_s=4$  system represents the lower density region and expectedly less separated energy levels.

We recall the definitions

$$IP = E_{(N-1)} - E_N,$$

$$EA = E_N - E_{(N+1)}.$$

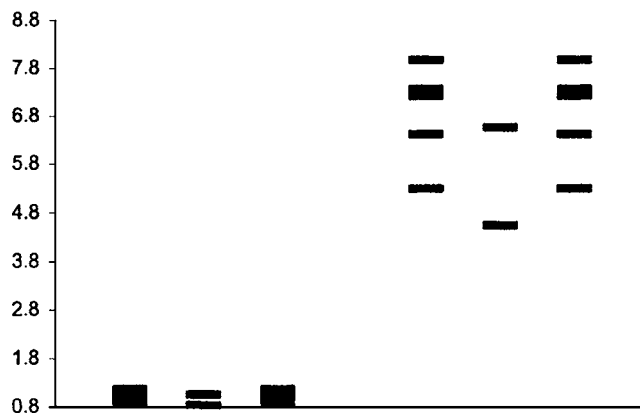


FIG. 3. Parabolic eigenvalue spectrum for  $N=6$  dot at (a)  $r_s=4$  and (b)  $r_s=0.75$ . Energy is calculated in Hartree atomic units.

Figure 4 shows the ionization potentials (IPs) of 2, 6, and 12 electron systems. As expected, the difference between the energy levels and the IPs increases with the number of electrons for a fixed value of  $\omega$ . It must also be noted that in highly correlated systems, change of the number of electrons does not affect the IPs, while in weakly correlated systems we see the reverse result.

Singlet excitations are also studied and the excitation energies are calculated for  $N=2$  and 6 by varying the value of  $r_s$ . Figure 5 shows the first singlet excitations for two and six electron dots. Excitations are  $1s \rightarrow 2p$ ,  $1s \rightarrow 3d$ , and  $1s \rightarrow 3s$  for a two electron dot and  $2p \rightarrow 3d$ ,  $2p \rightarrow 3s$ , and  $2p \rightarrow 4f$  for a six electron dot. The excitation energies for different size quantum dots have been calculated by the EOMCC method previously.<sup>24</sup> However, these have been done using Gaussian basis sets of varying size. For indicative comparison, we reproduce in Table III the lowest three EOMCC singlet excitations for two-electron quantum dots using 60 Gaussian basis containing  $s, p, d$  and  $f$  functions and the corresponding FSMRCC results for different values of  $\omega$ . The FSMRCC results presented are in a  $60 \times 60$  grid. We find very good agreement of the results.

Turning our attention to the FSMRCC results, we observe that the rate of change in excitation energy with respect to  $r_s$  must also be noted. In both  $N=2$  and  $N=6$  electron dots, by increasing the  $r_s$  beyond  $r_s=1.5$  and shifting to the high density region, the excitation energies are not affected much. Recall the eigenvalue spectra and the increase in energy level separations by decreasing the value of  $r_s$ . As expected, it is observed that the excitation energy decreases by increasing the value of  $r_s$ . On the other hand, in the weakly correlated

TABLE III. First three singlet excitation energies obtained by FSMRCC ( $60 \times 60$  grid (basis) and EOMCC (60 basis functions) as in Ref. 24. All energies are in Hartree atomic units.

$\omega$	$1s \rightarrow 2p$		$1s \rightarrow 3d$		$1s \rightarrow 3s$	
	FSMRCC	EOMCC	FSMRCC	EOMCC	FSMRCC	EOMCC
0.4	0.402	0.402	0.464	0.507	0.737	0.731
0.6	0.627	0.603	0.759	0.815	1.102	1.102
0.8	0.798	0.803	1.007	1.131	1.443	1.475
1.0	0.998	1.004	1.298	1.456	1.801	1.850

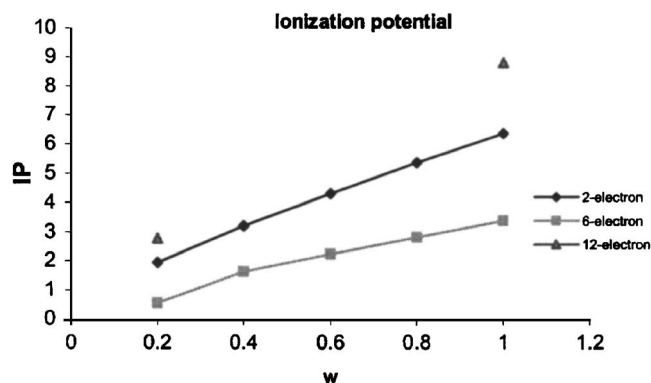


FIG. 4. The IP energies for  $N=2$ , 6, and 12 electron quantum dots at different values of  $\omega$ . Energies are measured in effective Hartree atomic units.

region (high values of  $r_s$ ), the excitation energy is not sensitive to the number of electrons. Indeed in this region the mean field description is valid. Figures 6(a) and 6(b) show the charge density of a six electron system at two values of  $r_s=1$  and  $r_s=4$ . The densities are calculated using the HF and CC methods. CC charge density includes correlation effect and it can be seen that the charge density is lower in height due to the distribution of charge in virtual space. As expected, it is seen that density decreases dramatically by increasing  $r_s$ . This effect can be seen more clearly in Fig. 6(c) where charge density is plotted for a six electron dot by varying the value of  $r_s$  from  $r_s \sim 0.7$  to  $r_s \sim 4$ .

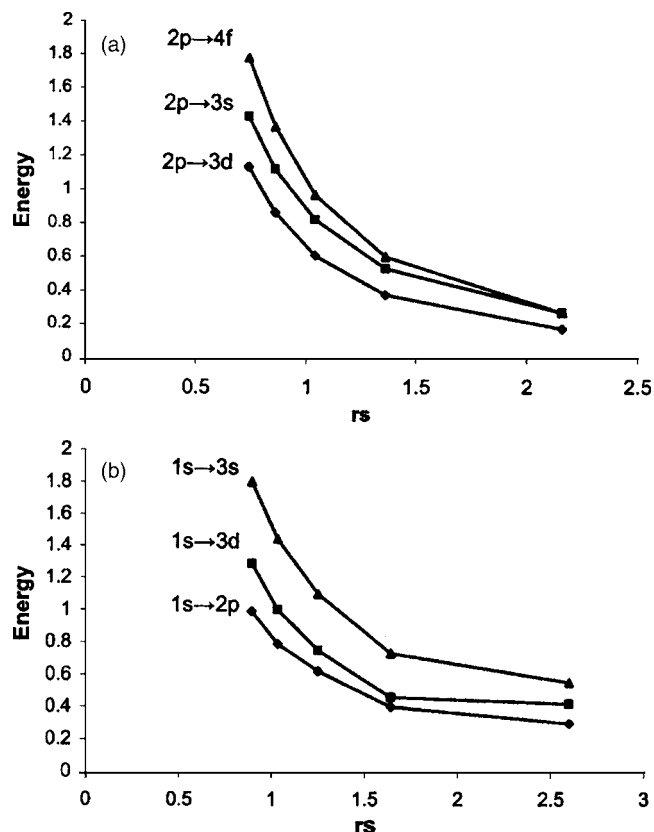


FIG. 5. The first three excitation energies for (a)  $N=6$  and (b)  $N=2$  electron quantum dots at different values of  $r_s$ . Energies are measured in effective Hartree atomic units.

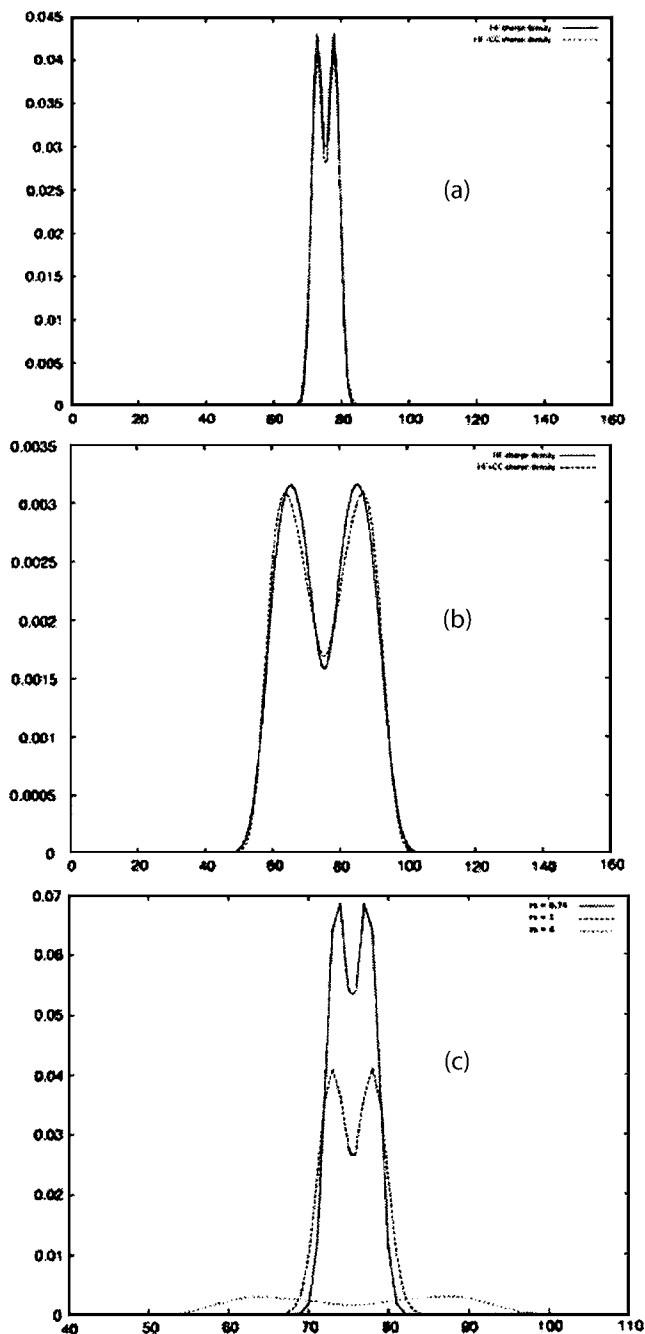


FIG. 6. HF and CC charge densities are plotted along the diameter of a six electron quantum dot at (a)  $r_s=1$  and (b)  $r_s=4$ . (c) shows the CC charge density at  $r_s=0.7$ ,  $r_s=1$ , and  $r_s=4$  for a  $N=6$  electron quantum dot.

## V. CONCLUSION

We have investigated the electronic structure of parabolically confined quantum dots with 2, 6, 12, and 20 electrons. We use the explicitly well established CCSD and MRCC methods. We calculated the ground state, correlation energy, ionization potential, and electron affinity as well as excitation energy. Excitation energies are compared with indicative EOMCC results and the agreement is quite good. Our study shows the potential of extensive and highly correlated CCSD and MRCCSD methods in treating a large number of electrons for two-dimensional interacting confined systems. Study of satellite structures in the electron detachment and

excitation spectrum would be of great future interest in terms of comparison of FSMRCC with EOMCC, where higher excitations (i.e., two hole–one particle space for IP and two hole–two particle space for EE) have to be treated almost on the same footing. However, our present study for main IPs and EEs show good correlation of the FSMRCC and EOMCC results.

## ACKNOWLEDGMENTS

The authors would like to thank S. A. Blundell for Poisson equation solver and S. Krishnamurthy and P. U. Manohar for discussions and supports. Two of the authors (B.S.P. and D.G.K.) are grateful to the Indo-French Center of the Promotion of Advanced Research (India)/Center Franco-Indian Pour la Promotion de la Recherche Avancé (France) for the partial financial assistance for the project.

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