



Electron correlation in artificial atoms

Thomas M. Henderson, Keith Runge, Rodney J. Bartlett *

Quantum Theory Project, University of Florida, Gainesville, FL 32611, USA

Received 14 November 2000; in final form 16 January 2001

Abstract

Electron correlation is essential to the accurate description of molecular systems. Here, parabolic quantum dots (often referred to as artificial atoms) are treated with the coupled cluster formalism of quantum chemistry to introduce correlation. Electron correlation is shown to account for between 1% and 9% of the total energy of quantum dots with from two to eight electrons and has a significant qualitative effect on the addition spectra. We employ a scaling relationship, confirmed by our calculations, which allows the treatment of quantum dots without specific reference to material properties. © 2001 Elsevier Science B.V. All rights reserved.

Semiconductor quantum dots [1,2] have attracted tremendous interests, both experimentally and theoretically, in the past several years. Between two layers of one semiconductor is placed a thin layer of a second semiconductor; this thin layer, a few nanometers in thickness and tens to hundreds of nanometers across, comprises the quantum dot. Excess electrons are driven into the dot by an overpotential, where they are being essentially confined to two dimensions.

Quantum dots have often been called ‘artificial atoms’ because they share some of the properties of real atoms. They have discrete electronic spectra with narrow line widths and degenerate energy levels. Artificial atoms exhibit lasing [3], just as real atoms do. Their level structure makes it possible to build a periodic table of artificial atoms, and bonding between artificial atoms has been observed [4]. With a vast array of potential uses, ranging from applications in quantum computers

through the creation of so-called ‘designer solids’ plus use in lasers and other optical or electronic devices, a rigorous, many-electron, theoretical understanding of these systems is critical for optimum design control.

Most theoretical treatments of quantum dots assume they constitute a two-dimensional system and treat the electron–electron interaction via the constant interaction model [5]. Attempts to go beyond this model have typically used Hartree–Fock (HF) [6–8], exact diagonalization (ED) [8–14], or density functional theory (DFT) [15,16]. HF fails entirely to describe electron correlation, can easily treat only the lowest energy state of a given symmetry, and unrestricted HF often improperly describes spin for open-shell systems. DFT, which attempts to indirectly introduce some electron correlation via a wide variety of exchange–correlation potentials, has similar spin and symmetry problems for open-shell systems and does not provide a path to converge to the exact answer. ED is computationally intractable for larger systems. Therefore, it seems desirable to establish a theoretical framework that provides an accurate

* Corresponding author. Fax: +1-352-392-8722.

E-mail address: bartlett@qtp.ufl.edu (R.J. Bartlett).

treatment of correlation and spin for ground and excited states while remaining computationally practical for many-electron artificial atoms. Here, we report the application of coupled cluster (CC) methods [17,18] which are easily applied in either two or three dimensions and for ‘artificial molecules’, since there is no assumption of cylindrical or spherical symmetry, to treat electron correlation in quantum dots to a very high level of approximation.

It has long been understood that electron correlation is of critical importance in atoms, molecules, and solids, and it should also be in quantum dots. However, the methods must be efficient enough computationally to allow the treatment of many electron systems. It is also essential that the correlation approach scale properly with the number of electrons, that is, it must be ‘size-extensive’. Furthermore, it is desirable to treat excited states to a similar degree of accuracy. Here, aided by a scaling relationship that allows quantum dots to be described like real atoms, we demonstrate the application of the highly accurate CC methodology to artificial atoms.

The basic CC ansatz is that the wave function is written as an exponential excitation operator onto an independent particle reference,

$$|\Psi_{\text{CC}}\rangle = e^T |\Phi_0\rangle, \quad (1)$$

where T takes the form

$$T = \sum_p^N T_p, \quad (2)$$

$$T_n = \frac{1}{(n!)^2} \sum_{\substack{ijk\dots \\ abc\dots}} t_{ijk\dots}^{abc\dots} a^\dagger i b^\dagger j c^\dagger k \dots$$

with $a^\dagger i$ exciting an electron from the i th occupied orbital into the a th virtual orbital. While the reference is normally taken to be HF, this need not be the case. The CC ansatz leads to an energy expression of the form

$$E = \langle \Phi_0 | \bar{H} | \Phi_0 \rangle, \quad (3)$$

where

$$\bar{H} = e^{-T} H e^T. \quad (4)$$

The $t_{ijk\dots}^{abc\dots}$ are given by

$$\langle \Phi_{ijk\dots}^{abc\dots} | \bar{H} | \Phi_0 \rangle = 0, \quad (5)$$

where $|\Phi_{ijk\dots}^{abc\dots}\rangle$ corresponds to the determinant

$$|\Phi_{ijk\dots}^{abc\dots}\rangle = a^\dagger i b^\dagger j c^\dagger k \dots | \Phi_0 \rangle. \quad (6)$$

Limiting the T excitation operator to single and double excitations ($T = T_1 + T_2$) defines the coupled cluster singles and doubles (CCSD) [19] method used in this work.

The CC formalism has several advantages in its treatment of electron correlation. First, it provides quite high accuracy, with CCSD typically recovering about 93% of the correlation energy in molecular systems [18]. At the same time, it is sufficiently computationally efficient to allow for the treatment of reasonably sized systems, with routine application to systems with tens of electrons [18]. It is a size-extensive method (i.e., the energy contains no unlinked diagrams), and hence the energy and wave function scale properly with the number of electrons. Furthermore, the results are insensitive to the choice of reference orbitals, which often makes it possible to treat difficult problems accurately using non-standard references [20]. CC methods are usually able to correct the spin-contamination and other symmetry-breaking problems often found in unrestricted HF (UHF) [21]. Although a CCSD based on a UHF reference does not give a spin eigenfunction, it is much closer than is the UHF [21]. Excited, ionized, and electron-attached states can be described within the equation-of-motion coupled cluster (EOM-CC) framework [22,23], and it is possible to make accurate predictions about a wide range of properties, ranging from spin densities [24] to hyperpolarizabilities [25] so that, for example, predictions about quantum dot lasers can be made.

In order to facilitate this research, we take advantage of a convenient property of the quantum dot Hamiltonian. Introducing the scaling relationship

$$\rho_i = \frac{m^*}{\kappa} r_i, \quad (7)$$

we can reduce the number of effective parameters in the problem from four to two. Then the Hamiltonian for a quantum dot is

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

It can easily be shown that

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

where

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

This makes it possible to treat harmonically confined electrons over wide ranges of frequencies within our framework. Further, with typical material constants ($m^* = 0.067$ and $\kappa = 12.4$), frequencies of interest ($\omega = 0.18$ mH) scale into a range more typical of atomic and molecular systems ($\omega' = 0.42$ H), where traditional quantum chemical techniques and basis sets can be readily applied.

In order to calibrate the method and choice of basis set, we present a few sample results for two electron systems (for which the exact solutions can be found in both two [26,27] and three [28,29] dimensions). The exact solutions can be readily found only for a discrete set of frequencies, but for arbitrary materials constants; the eigenvalues reported below were obtained in this manner and explicitly obey the scaling relationship, which was not used to find them. In each case in Table 1, successive pairs of entries correspond to the same solution for two different sets of materials constants (and hence of different frequencies). We also report the ratio of the energy at $m^* = \kappa = 1$ to that

at the other set of materials constants as the value R , with R_{exact} being the R value predicted by the scaling relationship (as this value appears in the solution of the Schrödinger equation).

CCSD is exact for two electron systems; thus, all error in these calculations is due to basis set effects. As can be seen, the basis set chosen yields an energy accurate to about 0.1% in two dimensions; this basis set contains cartesian Gaussians of s-, p-, d-, and f-types, with exponents of $0.05 m^* \omega$, $0.1 m^* \omega$, $0.2 m^* \omega$, $0.4 m^* \omega$, $0.6 m^* \omega$, $m^* \omega$, and $2 m^* \omega$. (This basis set is constructed in an even-tempered manner[30].) After removing the near-linear dependencies, this amounts to 60 functions in two dimensions, or 127 functions in three. Also, it is noteworthy that while the CCSD results are worse in two dimensions than they are in three, they are still quite good, while the HF results are much poorer in two dimensions than in three. Finally, note that the scaling relationship is numerically verified by both HF and CCSD.

The need for correlated methods in molecular systems is clear; it may in fact be greater in artificial atoms. An examination of Fig. 1 shows that as a fraction of the total energy, the correlation energy remains significant (a few percent of the total energy) even as the number of electrons in the system becomes larger. Note that the correlation energy may be numerically quite substantial for large systems even when it constitutes only 1% of the total energy. Further, as the confining frequency becomes lower, the correlation energy becomes more important. Clearly, if one wants accurate energies and properties, correlation effects are critical.

Table 1
Results for basis set and scaling calibrations in both two and three dimensions^a

m^*	κ	ω	N_{Dim}	E_{SCF}	E_{CCSD}	E_{exact}	R_{SCF}	R_{CCSD}	R_{exact}
1	1	1	2	3.1619	3.0032	3	50.000	50.000	50
0.5	5	0.02		0.0632	0.0601	0.06			
1	1	0.1667	2	0.7687	0.6671	0.6667	6.667	6.667	$\frac{6}{3}$
0.6	2	0.025		0.1153	0.1001	0.10			
1	1	0.5	3	2.0384	2.0003	2	25.000	25.000	25
0.16	2	0.02		0.0815	0.0800	0.08			
1	1	0.1	3	0.5290	0.5001	0.5	12.500	12.500	12.5
0.32	2	0.008		0.0423	0.0400	0.04			

^a All numbers are given in hartree atomic units.

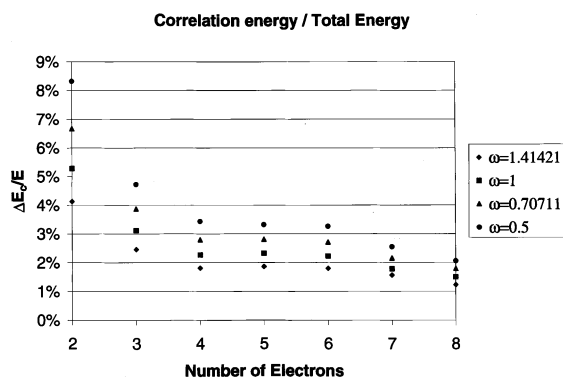


Fig. 1. Correlation energy as a fraction of total energy for a quantum dot in the absence of a magnetic field. Frequencies are measured in hartree atomic units and $m^* = \kappa = 1$.

This can also be seen by examining the addition spectra in the absence of a magnetic field, the results for which are summarized in Table 2. Fig. 2 shows the addition spectrum at the HF and CCSD levels, with $m^* = \kappa = \omega = 1$. In HF, $\mu(5)$ and $\mu(6)$ are about 100 mH too high as compared to the CCSD results; this represents an error of about 2%. This actually changes the character of the spectrum. It shows too strong a peak at the half-filled p-level ($n = 5$) and too weak a peak at the onset of the d-level ($n = 7$).

These effects become more pronounced as the binding frequency becomes lower and correlation becomes more important. Fig. 3 shows the HF and CCSD addition spectra for the same set of material constants as Fig. 2, but with $\omega = 1/2$. Again, $\mu(5)$ and $\mu(6)$ are about 100 mH too high, an error of about 3%. More significantly, the qualitative character of the HF spectrum now shows no ‘magic number’ at $n = 6$, while this is still easily seen in the CCSD results. Correlation thus has a profound effect even in the addition spectrum, where one might expect it to be less important,

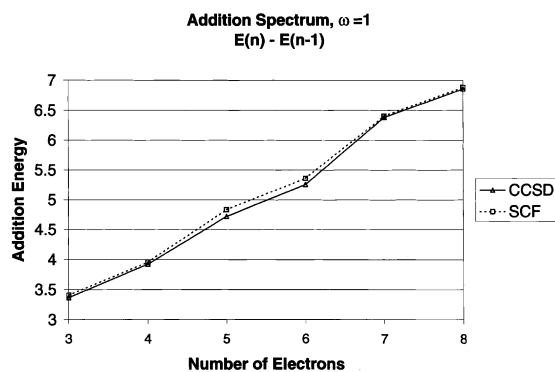


Fig. 2. Addition spectrum for a quantum dot in the absence of a magnetic field at frequency $\omega = 1$ a.u. Energies are also measured in hartree atomic units and $m^* = \kappa = 1$.

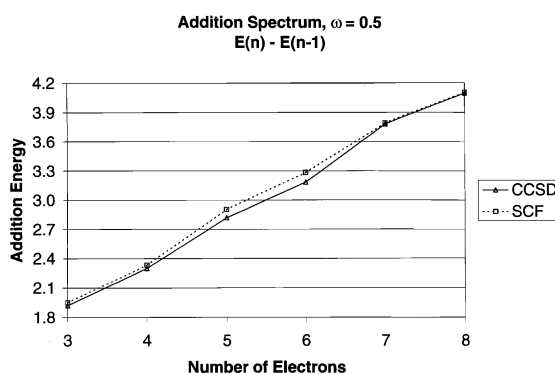


Fig. 3. Addition spectrum for a quantum dot in the absence of a magnetic field at frequency $\omega = 0.5$ a.u. Energies are measured in hartree atomic units and $m^* = \kappa = 1$.

since the errors made by ignoring correlation might be expected to partially cancel in these cases.

In summary, we demonstrate the application of the CCSD formalism to artificial atoms. We also develop a basis set which allows for basis-set error on the order of 0.10% in these calculations. Correlation effects are shown to be signif-

Table 2
Addition energies for two-dimensional quantum dots for two frequencies^a

ω	Method	$\mu(3)$	$\mu(4)$	$\mu(5)$	$\mu(6)$	$\mu(7)$	$\mu(8)$
1.0	HF	3.404	3.956	4.836	5.361	6.407	6.884
	CCSD	3.364	3.921	4.722	5.259	6.385	6.856
0.5	HF	1.951	2.332	2.905	3.284	3.793	4.103
	CCSD	1.920	2.299	2.818	3.185	3.782	4.096

^a Energies are given in hartree atomic units, and $\mu(N)$ is defined as $E(N) - E(N - 1)$.

icant, having a particular effect on the addition spectrum. We also show that the method obeys a scaling relationship which obviates the need to explicitly consider the material constants of the dot.

Acknowledgements

The authors would like to thank professors Uzi Landmann and Hai-Ping Cheng for bringing this problem to our attention. This work has been supported by the National Science Foundation under grant No. DMR-9980015.

References

- [1] R.C. Ashoori, *Nature* 379 (1996) 413.
- [2] N.F. Johnson, *J. Phys. Condens. Matter* 7 (1995) 965.
- [3] N.N. Ledentsov, V.M. Ustinov, V.A. Schchukin, P.S. Kopiev, Z.I. Alferoz, D. Bimberg, *Semiconductors* 32 (1998) 343 1998.
- [4] G. Schedelbeck, W. Wegscheider, M. Bichler, G. Abstreiter, *Science* 278 (1997) 1792.
- [5] R.C. Ashoori, H.L. Stormer, J.S. Weiner, L.N. Pfeiffer, K.W. Baldwin, K.W. West, *Phys. Rev. Lett.* 71 (1993) 613.
- [6] C.de.C. Chamon, X.G. Wen, *Phys. Rev. B* 49 (1994) 8227.
- [7] C. Yannouleas, U. Landmann, *Phys. Rev. Lett.* 82 (1999) 5325.
- [8] D. Pfannkuche, V. Gudmundsson, P.A. Maksym, *Phys. Rev. B* 47 (1993) 2224.
- [9] P.A. Maksym, T. Chakraborty, *Phys. Rev. B* 45 (1992) 1947.
- [10] J.J. Palacios, L. Martin-Moreno, G. Chiappe, E. Louis, C. Tejedor, *Phys. Rev. B* 50 (1994) 5760.
- [11] M. Wagner, U. Merkt, A.V. Chaplik, *Phys. Rev. B* 45 (1992) 1951.
- [12] J.M. Kinaret, Y. Meir, N.S. Wingreen, P.A. Lee, X.G. Wen, *Phys. Rev. B* 46 (1992) 4681.
- [13] P. Hawrylak, *Phys. Rev. Lett.* 71 (1993) 3347.
- [14] S.R. Eric Yang, A.H. MacDonald, M.D. Johnson, *Phys. Rev. Lett.* 71 (1993) 3194.
- [15] S. Nagaraja, J.P. Leburton, R.M. Martin, *Phys. Rev. B* 60 (1999) 8759.
- [16] K. Hirose, N.S. Wingreen, *Phys. Rev. B* 59 (1999) 4604.
- [17] R.J. Bartlett, in: D.R. Yarkony (Ed.), *Modern Electronic Structure Theory*, World Scientific, Singapore, 1995.
- [18] R.J. Bartlett, J.F. Stanton, in: D. Boyd, K. Lipkowitz (Eds.), *Reviews in Computational Chemistry* 5, VCH, New York, 1994.
- [19] G.D. Purvis, R.J. Bartlett, *J. Chem. Phys.* 76 (1982) 1910.
- [20] J.D. Watts, R.J. Bartlett, *J. Chem. Phys.* 95 (1991) 6652.
- [21] G.D. Purvis, H. Sekino, R.J. Bartlett, *Coll. Czech. Chem. Commun.* 53 (1988) 2203.
- [22] D.C. Comeau, R.J. Bartlett, *Chem. Phys. Lett.* 207 (1993) 414.
- [23] J.F. Stanton, R.J. Bartlett, *J. Chem. Phys.* 98 (1993) 729.
- [24] S.A. Perera, J.D. Watts, R.J. Bartlett, *J. Chem. Phys.* 100 (1994) 1425.
- [25] H. Sekino, R.J. Bartlett, *Chem. Phys. Lett.* 234 (1995) 87.
- [26] M. Dineykhon, R.G. Nazmitdinov, *Phys. Rev. B* 55 (1997) 13707.
- [27] J.L. Zhu, Z.G. Li, J.Z. Yu, K. Ohno, Y. Kawazoe, *Phys. Rev. B* 55 (1997) 15819.
- [28] S. Kais, D.R. Herschbach, R.D. Levine, *J. Chem. Phys.* 91 (1989) 7791.
- [29] M. Taut, *Phys. Rev. A* 48 (1993) 3561.
- [30] K. Rudenberg, R.C. Raffanetti, R.D. Bardo, in: D.W. Smith (Ed.), *Proceedings of the 1972 Boulder Seminar Research Conference on Theoretical Chemistry*, Wiley, New York, 1973.