

Excited states in artificial atoms via equation-of-motion coupled cluster theory

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Excited, ionized, and electron attached states of parabolic quantum dots (often referred to as artificial atoms) are treated with the equation-of-motion coupled cluster theory. Collective excitations are often important, implying the need for accurate inclusion of correlation effects in excitation spectra.

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I. INTRODUCTION

During the past several years, semiconductor quantum dots¹⁻⁴ have attracted tremendous interest, both experimentally and theoretically. 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 essentially confined to two dimensions (2D).

Quantum dots have often been called “artificial atoms” because they share some of the properties of real atoms, such as degenerate level structure and discrete spectra with relatively narrow lines. Among other things, artificial atoms exhibit lasing, just as real atoms do.⁵ Hence, the design of devices built upon quantum dots is of great interest. However, such design requires a coordinate, predictive theoretical description of the properties of quantum dots, in their ground as well as excited states. For an electronic structure theory to be predictive, it is necessary that it properly include the effects of electron correlation. Previous work has demonstrated the essential effects of electron correlation on ground states, using coupled-cluster⁶ and quantum Monte Carlo^{7,8} methods. Here, we wish to address the issue of electron correlation in excited and ionized states.

Direct attempts to access excited states computationally by using traditional ground-state methods are hampered by the need to make the excited states orthogonal to all lower states. Typically, such direct computations are limited to the lowest state of a given spin and spatial symmetry, and accessing other states, such as the higher states of the same symmetry, requires more advanced techniques. These methods for treating excited states include exact diagonalization when applicable,^{9,10} time-dependent density functional theory,¹¹⁻¹⁴ and time-dependent Hartree-Fock theory.^{15,16} Exact diagonalization is limited to very few electrons. Time-dependent density functional theory suffers from an unknown frequency-dependent (or in the adiabatic approximation, static) exchange-correlation functional, making it impossible to be “predictive” in the sense of converging to the exact answer. Time-dependent Hartree-Fock (HF) theory (equivalent to the random phase approximation) has no electron correlation effects, and these are required for an accurate treatment; electron correlation must be included in any predictive theory of excited states.

Hence, we use the highly correlated equation-of-motion coupled cluster¹⁷ (EOM-CC) method, the excited-state

complement to our previous ground-state studies.⁶ This method is designed to treat excited states accurately and falls within the widely used family of coupled-cluster methods.^{18,19} With a suitable basis set of Gaussian functions, it is well known that in terms of accuracy, ground-state electronic structure calculations generally follow the pattern HF < MBPT(2) < CCSD < CCSDT < full CI, where MBPT(2) is second-order many-body perturbation theory and CCSD means coupled-cluster theory limited to single and double excitations, while T indicates inclusion of triple excitations as well. The full configuration interaction (CI) corresponds to the N -electron excited limit and is the best possible solution in the basis set. Similarly, for excited, ionized, and electron attached states, we have a coordinate paradigm of converging accuracy, CIS < EOM-MBPT(2) < EOM-CCSD < EOM-CCSDT < full CI. Here, CIS is the configuration interaction limited to single excitations (also known as the Tamm-Dancoff approximation), and EOM- X indicates the EOM based upon a ground-state wave function of type X .

In the coupled cluster formalism, the ground-state correlated wave function is written as an exponential wave operator acting on a single-particle reference, such as a Hartree-Fock or Kohn-Sham determinant:

$$|\Psi\rangle = e^T |\Phi_0\rangle, \quad (1)$$

where T is of the form

$$T = \sum_{n=1}^N T_n, \quad (2)$$

$$T_n = \frac{1}{(n!)^2} \sum_{\substack{i_1 \dots i_n \\ a_1 \dots a_n}} t_{i_1 i_2 \dots i_n}^{a_1 a_2 \dots a_n} a_1^\dagger i_1 a_2^\dagger i_2 \dots a_n^\dagger i_n, \quad (3)$$

and $a^\dagger i$ excites an electron from the i th occupied orbital to the a th virtual orbital. To describe excited states, we introduce the operator

$$R_k = (r_k)_0 + \sum (r_k)_i^a a^\dagger i + \sum (r_k)_{ij}^{ab} a^\dagger i b^\dagger j + \dots = (R_k)_0 + (R_k)_1 + (R_k)_2 + \dots \quad (4)$$

Then inserting the wave function ansatz

$$|\Psi_k\rangle = R_k e^T |\Phi_0\rangle \quad (5)$$

into the Schrödinger equation, we obtain

$$e^{-T}[H, R_k]e^T|\Phi_0\rangle = [\bar{H}, R_k]|\Phi_0\rangle = (E_k - E_0)e^{-T}R_k e^T|\Phi_0\rangle \equiv \varepsilon_k R_k|\Phi_0\rangle. \quad (6)$$

By diagonalizing the coupled-cluster effective Hamiltonian

$$\bar{H} = e^{-T} H e^T \quad (7)$$

in the space of determinants defined by the truncation of the R operator, we obtain the right- and left-hand amplitudes and the eigenvalues. Limiting the T operator to $T_1 + T_2$ defines the coupled-cluster singles and doubles²⁰ model for the ground state and with R truncated after double excitations yields the equation-of-motion coupled-cluster singles and doubles²¹ model for the excited states (used in most of this work), in which the effective Hamiltonian is diagonalized in the space of singly and doubly excited determinants. Adding the initial triple excitation terms to T_2 and R_3 gives the EOM-CCSDT-3 method.²² Since \bar{H} is non-Hermitian, in addition to the right-hand eigenvector R_k , we have a left-hand eigenvector

$$\langle\Phi_0|L_k\bar{H} = \langle\Phi_0|L_k\varepsilon_k, \quad (8)$$

with the same eigenvalue ε_k . We choose the normalization

$$\langle\Phi_0|L_i R_j|\Phi_0\rangle = \delta_{ij}. \quad (9)$$

For the ground state, L_0 is $1 + \Lambda$ and R_0 is 1. Here, Λ is just that operator which makes the coupled-cluster energy stationary to variation in the t amplitudes (t_i^a , etc.) and is expanded as

$$\Lambda = \sum_{n=1}^N \Lambda_n, \quad (10)$$

$$\Lambda_n = \frac{1}{(n!)^2} \sum_{\substack{i_1 \dots i_n \\ a_1 \dots a_n}} \lambda_{i_1, i_2, \dots, i_n}^{a_1, a_2, \dots, a_n} i_1^\dagger a_1 i_2^\dagger a_2 \dots i_n^\dagger a_n, \quad (11)$$

and the expansion in Λ_n is truncated in the same way as the expansion in T_n , which is in fact the leading contribution to Λ_n^\dagger .

There are many extensions to the standard equation-of-motion approach. By modification of the expansion of the EOM operators L_k and R_k for the effective Hamiltonian, one can directly study electron attachment and removal processes through the EA-EOM (Ref. 23), and IP-EOM (Ref. 24) variant methods, respectively. The latter can be viewed as arising from allowing excited orbital a to be in the continuum, which thereby reduces the amplitudes of the R operator to r_i and r_{ij}^b ; EA-EOM is the reverse, with amplitudes r^a , r_i^{ab} , etc.

From the left and right eigenvectors for the effective Hamiltonian, one can evaluate properties conveniently via, for example,²¹ the transition densities, or when $p = q$, density matrices for the p th state:

$$\rho_{pq}(\mathbf{r}) = \langle\Phi_0|L_p e^{-T} \left(\sum_{i=1}^{N_e} \delta(\mathbf{r} - \mathbf{r}_i) \right) e^T R_q|\Phi_0\rangle. \quad (12)$$

The model Hamiltonian for a quantum dot is^{1,4}

$$H(m^*, \kappa, \omega) = \sum_{i=1}^N \frac{p_i^2}{2m^*} + \frac{1}{2} m^* \omega^2 \sum_{i=1}^N r_i^2 + \frac{1}{\kappa} \sum_{i < j=1}^N \frac{1}{r_{ij}}, \quad (13)$$

where the electrons are confined to two dimensions, and the material constants m^* (the effective mass) and κ (the dielectric constant) are scaled from the problem by making use of the relationship

$$E(m^*, \kappa, \omega) = E(1, 1, \omega'), \quad (14)$$

$$\omega' = \frac{\kappa^2}{m^*} \omega.$$

Thus, we will present results only for $m^* = \kappa = 1$, with the confining frequency treated as the fundamental parameter. In these units, the energy is measured in effective hartrees E_H^* . Typical values of the materials constants are $m^* = 0.067m_e$ and $\kappa = 12.4$ (GaAs), and $\hbar\omega$ is usually on the order of a few meV; when scaled into effective atomic units, this gives a frequency ω' on the order of 0.1–1 effective hartrees. In terms of the dimensionless parameter

$$\lambda = \frac{e^2 / (\kappa l_0)}{\hbar \omega}, \quad (15)$$

$$l_0 = \sqrt{\frac{\hbar}{m^* \omega}},$$

which is the ratio of the characteristic Coulombic and harmonic energies, we have the scaled relationship

$$\lambda = \frac{1}{\sqrt{\omega}}, \quad (16)$$

so that our calculations cover a range of λ between 1 and about 1.83.

We consider three basis sets in this work; all consist of Cartesian Gaussians. Our standard basis set contains functions of s , p , d , and f type (due to cylindrical symmetry, these correspond to Σ , Π , Δ , and Φ functions, respectively, with g functions denoted by Γ), with exponents of $0.05m^*\omega$, $0.1m^*\omega$, $0.2m^*\omega$, $0.4m^*\omega$, $0.6m^*\omega$, $m^*\omega$, and $2m^*\omega$. To assess the importance of g functions, we add them with exponents of $0.1m^*\omega$, $0.2m^*\omega$, $0.4m^*\omega$, $0.6m^*\omega$, and $m^*\omega$. Finally, for computational ease, we remove the smallest and largest exponents for the s -, p -, d -, and f -type functions and add just two g functions, with exponents of $0.4m^*\omega$ and $0.6m^*\omega$. These basis sets do have near linear dependences, and following a transformation based upon eigenvalues of the overlap matrix, the nearly linearly dependent combinations of basis functions are simply dropped from the calculation. Once this is done, our basis sets consist of 60, 77, and

TABLE I. Ground- and first four singlet excited-state energies of a 2-electron dot from variational calculation and from CCSD and EOM-CCSD.

ω	Ground		$1s \rightarrow 2p$		$1s \rightarrow 3d$		$1s \rightarrow 3s$		$1s^2 \rightarrow 2p^2$	
	var	CC	var	EOM	var	EOM	var	EOM	var	EOM
0.3	1.082	1.083	1.382	1.384	1.447	1.447	1.627	1.629	1.682	1.687
0.4	1.376	1.377	1.776	1.779	1.887	1.887	2.105	2.108	2.176	2.179
0.5	1.660	1.662	2.160	2.164	2.322	2.322	2.574	2.577	2.660	2.665
0.6	1.937	1.939	2.537	2.542	2.753	2.754	3.036	3.041	3.137	3.143
0.7	2.209	2.211	2.909	2.914	3.183	3.183	3.494	3.499	3.609	3.615
0.8	2.476	2.479	3.276	3.282	3.610	3.610	3.948	3.954	4.076	4.083
0.9	2.740	2.742	3.640	3.646	4.035	4.035	4.399	4.405	4.540	4.548
1.0	3.000	3.003	4.000	4.007	4.459	4.459	4.847	4.853	5.000	5.009

50 functions, respectively. All computations used the ACES II program system,²⁵ with the VMOL integral package modified to generate the appropriate two-dimensional integrals.

II. BASIS SET ASSESSMENT

A. Two-electron dot

To help assess the basis set error in the excitation energies, we examine 2-electron dots. Since both the ground-state CCSD and excited-state EOM-CCSD are formally exact for 2-electron systems, the error in these calculations must be due entirely to basis set. In order to generate essentially exact, basis-set-independent results, we make simple variational estimates of the first several eigenstates in the following manner.

For a 2-electron dot, the Hamiltonian is separable into center-of-mass and relative coordinates. The center-of-mass Hamiltonian is a simple harmonic oscillator, while the relative Hamiltonian is

$$-\nabla^2 + \frac{1}{4}\omega^2 r^2 + \frac{1}{r}. \quad (17)$$

After separating out the angular part $e^{im\phi}$ (note that the quantum number m controls the particle exchange symmetry of the spatial part of the wave function and hence controls the spin; singlet states have even m and triplet states have odd m), we are left with a one-dimensional eigenvalue problem

$$-\frac{1}{r} \frac{d}{dr} \left(r \frac{d}{dr} \psi_{rad} \right) + \left(\frac{1}{4}\omega^2 r^2 + \frac{1}{r} + \frac{m^2}{r^2} - E_{rel} \right) \psi_{rad} = 0. \quad (18)$$

The long-range part of the solution is Gaussian with exponent $\frac{1}{4}\omega$, the short-range part is r^m , and the remainder of the wave function can be expanded in a power series as

$$1 + \frac{1}{1+2m} r + \alpha r^2 + \beta r^3 + O(r^4). \quad (19)$$

The exact wave function takes this form for known solutions of the model Hamiltonian (for example, with $\omega=1$, the exact ground-state solution takes the above form with $m=0$,

and with α , β , and all higher coefficients vanishing). We have found that using the coefficient α as our only variational parameter and taking $\beta=0$ for the ground state provides accuracy to about five decimal places, since adding a nonzero β as a second variational parameter changes the energy only at that level. The first excited-state is an excitation in the center-of-mass coordinate, with excitation energy ω , and the second singlet excitation energy is the lowest state with $m=2$, again estimated with $\beta=0$ and α as a variational parameter. The third excited state is another excitation in the interelectronic coordinate, this time with $m=0$. We therefore find α as the function of β that makes the ground-state and excited-state wave functions orthogonal, and treat β as the variational parameter. Finally, the fourth excited state is again an excitation in the center-of-mass coordinate, with excitation energy 2ω .

Using only s , p , d , and f functions, we show in Table I that the basis set error in the ground-state energy is a few mE_H^* only and the basis set error for the excited-state energies is about twice that for the lower excited states, a bit larger for the higher excited-states. Of course, the basis set error in the excited-state energy is expected to partially cancel with the basis set error in the ground-state energy, so that the excitation energies should be more accurate than the total energies. As seen in Table II, this is indeed the case; the errors in the excitation energies are comparable to the error in the ground-

TABLE II. First four singlet excitation energies of a 2-electron dot from variational calculation and from EOM-CCSD.

ω	$1s \rightarrow 2p$		$1s \rightarrow 3d$		$1s \rightarrow 3s$		$1s^2 \rightarrow 2p^2$	
	var	CC	var	EOM	var	EOM	var	EOM
0.3	0.300	0.301	0.365	0.364	0.545	0.546	0.600	0.604
0.4	0.400	0.402	0.511	0.507	0.729	0.731	0.800	0.802
0.5	0.500	0.502	0.662	0.660	0.914	0.915	1.000	1.003
0.6	0.600	0.603	0.816	0.815	1.099	1.102	1.200	1.204
0.7	0.700	0.703	0.974	0.972	1.285	1.288	1.400	1.414
0.8	0.800	0.803	1.134	1.131	1.472	1.475	1.600	1.604
0.9	0.900	0.903	1.295	1.293	1.659	1.663	1.800	1.806
1.0	1.000	1.004	1.459	1.456	1.847	1.850	2.000	2.006

state energy for the lower states, and while the error is somewhat larger for the more highly excited states, it remains well under $10mE_H^*$.

Thus, we see that even without g functions, the basis set used is adequate for lower excitation levels, with a basis set error on the order of a few mE_H^* . Incomplete treatment of correlation should be the main source of error for three or more electrons, at least until higher-angular-momentum functions start to make significant contributions to the wave function.

B. Influence of g functions

For quantum dots with more than 20 electrons, $g(\Gamma)$ functions must be included for even a qualitatively accurate Hartree-Fock calculation, as they begin to be occupied at that point. Of course, both correlated and excited-state calculations would require Γ functions for even fewer electrons. Thus, for higher excitations and for larger electron number, the basis set chosen might not be adequate. To assess this possibility, we expand our basis to include Γ -type functions. This adds substantially to the expense of the calculation; CCSD scales as $\approx n_{occ}^2 n_{virt}^4$, where n_{occ} and n_{virt} are the number of occupied and virtual orbitals, respectively, so that computations in the largest basis set used require about thrice the time of those in the middle basis set, which themselves require twice the time of computations in our smallest basis set. We therefore limit our results to 6 and 12 electrons, for the highest and lowest frequencies of interest ($\omega = 1E_H^*$ and $\omega = 0.3E_H^*$).

The inclusion of Γ functions has a substantial effect on the total ground-state energy for the 12-electron dot, lowering the estimate by a few tenths of an effective Hartree ($0.13E_H^*$ for $\omega = 0.3E_H^*$ and $0.18E_H^*$ for $\omega = 1E_H^*$), a number on the order of the lower excitation energies. As would be expected, the effect is not as pronounced in the 6-electron dot ($0.046E_H^*$ for $\omega = 0.3E_H^*$ and $0.053E_H^*$ for $\omega = 1E_H^*$), but is still sizable. This of course indicates that inclusion of higher-angular-momentum functions is important in describing properties of quantum dots with several electrons, though as we have seen, these functions are unnecessary for only a few electrons. The excitation energies are expected to be less sensitive to the omission of Γ functions than the total energies, due to partial cancellation of error.

Indeed, we find that adding Γ functions seems to have a fairly insignificant effect on the excitation energies for 6-electron dots, on the order of a few mE_H^* at $\omega = 0.3E_H^*$.

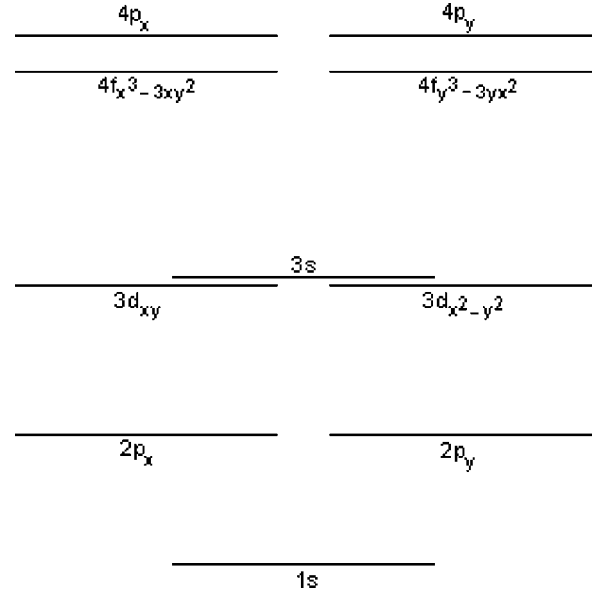


FIG. 1. Closed-shell Hartree-Fock orbital energy diagram.

Their influence is of course somewhat more pronounced for 12-electron dots, but remains under $10mE_H^*$ even at $\omega = 1E_H^*$, where the excitation energies are several tenths of an effective Hartree. Results are similar with the smallest basis set used (i.e., that with 50 basis functions).

Since adding Γ functions seems to have a fairly minimal impact on the excitation energies but increases the cost of the CCSD by a factor of almost 3, we concentrate on smaller basis sets in the rest of this work. In order to make contact with earlier work, we have also made only minimal use of the smallest basis set.

III. ORBITAL PICTURE

It is helpful in attempting to describe excited states to characterize them in terms of excitations out of mean-field orbitals. In Fig. 1, we give the orbital energy diagram for the closed-shell dot as a reference. Because the model one electron problem has the electron confined by a harmonic potential rather than by a Coulombic potential, the angular momenta for a principal quantum number n run from n down to zero, decreasing by steps of 2 instead of 1. Also, of course, there are only two functions of a given angular momentum and principal quantum number.

Note, however, that as customary in molecular theory, we

TABLE III. Representative excitation energies and AEL for the 12-electron dot.

$\omega = 0.3E_H^*$				$\omega = 1.0E_H^*$			
ϵ	Dominant excitations	AEL	$\ R_S\ $	ϵ	Dominant excitations	AEL	$\ R_S\ $
0.176	$3s \rightarrow 4p$	1.15	0.920	0.680	$3s \rightarrow 4f$	1.07	0.960
0.180	$3s \rightarrow 4f$	1.16	0.920	0.686	$3s \rightarrow 4p$	1.07	0.963
0.191	$3d \rightarrow 4f$	1.12	0.940	0.687	$3d \rightarrow 4f$	1.06	0.970
0.209	$3d \rightarrow 4p$	1.15	0.909	0.779	$3d \rightarrow 4p$	1.07	0.962
0.213	$3d \rightarrow 4p$ $3s \rightarrow 4f$	1.15	0.919	1.065	$3d \rightarrow 4f$ $3s \rightarrow 4p$	1.05	0.967

TABLE IV. Representative excitation energies and AEL for the 6-electron dot.

$\omega = 0.3E_H^*$				$\omega = 1.0E_H^*$			
ϵ	Dominant excitations	AEL	$\ R_S\ $	ϵ	Dominant excitations	AEL	$\ R_S\ $
0.089	$2p \rightarrow 3d$ $2p \rightarrow 3s$	1.11	0.937	0.499	$2p \rightarrow 3d$	1.05	0.969
0.120	$2p \rightarrow 3d$	1.09	0.948	0.561	$2p \rightarrow 3d$	1.04	0.975
0.154	$2p \rightarrow 3s$	1.18	0.891	0.682	$2p \rightarrow 3s$	1.08	0.952
0.166	$2p \rightarrow 3s$	1.22	0.876	0.719	$2p \rightarrow 3s$	1.11	0.946
0.190	$2p \rightarrow 3d$	1.20	0.887	0.734	$2p \rightarrow 3d$	1.10	0.946

use real basis functions; hence, for systems that differ by one electron from a closed subshell, cylindrical symmetry is lost unless the subshell being filled has zero angular momentum. Further, the orbital picture can be somewhat misleading in that naive application of Hund’s rule may predict the wrong spin state. For instance, Hund’s rule would predict that the 10-electron dot is a closed-shell singlet, but because the spin-spin interactions stabilize the triplet relative to the singlet, our calculations find that the triplet becomes the ground state for small enough confining frequencies (between $\omega = 0.3E_H^*$ and $0.4E_H^*$). On the other hand, we find that Hund’s rule does apply for the 4-electron dot, about which there has been some controversy, even at a frequency $\omega = 0.28E_H^*$ (corresponding to $\lambda = 1.89$).^{7,26}

IV. EFFECTS OF HIGHER EXCITATIONS

A. Onset of double-excitation character

When an excited state has significant double-excitation character, it is known for molecules that its description by the EOM-CCSD method becomes somewhat less accurate.^{26–28} (Of course, methods such as the time-dependent Hartree-Fock method and CI singles can be expected to fail.) Accordingly, it is important to discover when excited states start to exhibit substantial double-excitation character, so that a more advanced correlated ground-state treatment and correspondingly more sophisticated excited-state treatment can be used.

To help ascertain the importance of double excitations in a given excited state, we use two measures. One is the norm of the single-excitation part of the right eigenvector for the state of interest [explicitly, this is given by $\|R_S\|^2 = \sum (r_i^a)^2$; the remainder of the eigenvector is presumed to be constituted principally of double excitations] and the other is the approximate excitation level (AEL) metric of Stanton and Bartlett.²¹ This latter measure uses the right and left eigenvectors corresponding to the excited state of interest to estimate how many electrons are excited relative to the CC ground state. This is accomplished by examining the absolute difference between the diagonal parts of the ground-state and excited-state density matrices as represented in the natural orbitals that diagonalize the coupled-cluster ground-state density matrix. Singly excited states have an AEL number near 1, and as the AEL starts to rise above 1.1 or 1.2, double-excitation character becomes more important and the EOM-CCSD description becomes less reliable. By the time the AEL diagnostic nears 1.8 or 1.9, the state of interest would

be described as a nearly pure double excitation; the corresponding condition on $\|R_S\|$ is $\|R_S\| \approx 0$.

Unsurprisingly, we find that substantial double-excitation character is found in many fairly low-lying states for dots with weaker confining potential, and that as the confining potential becomes stronger, the double-excitation character decreases. In Table III, we provide results for a 12-electron dot, and in Table IV we do the same for a 6-electron dot; the column headed “Dominant excitations” describes the dominant transition(s) in the excited state as read from the right eigenvector.

In both cases, we see that the AEL is markedly lower for the higher frequencies, by somewhere between about 0.05 and 0.1, which are sizable numbers on the scale of the diagnostic. At the same time, the norm of the higher excitation part of the eigenvectors decreases by roughly a factor of 2. For the 12-electron dot at $\omega = 1E_H^*$, we find AEL numbers low enough (and single-excitation character in the eigenvectors high enough) that the EOM-CCSD excitation energies are most probably reliable. At the weaker confinement, however, the larger AEL numbers and lower single-excitation character indicate that some inclusion of triple excitations may be necessary for a proper description of these states. For the 6-electron dot, however, only the first few excited states even at the higher frequency are almost certainly reliable; even the fourth or fifth states up might require triple excitations in the ground-state reference. At the lower frequency of $\omega = 0.3E_H^*$, some inclusion of triples may be important for all the states and is almost certainly necessary for any but the first few excitations. As an aside, note that the lowest two excitations in the 12-electron dot at $\omega = 0.3E_H^*$ are reversed from the mean-field and CIS ordering, an indication of the importance of correlation.

TABLE V. Triples correction to correlation energy, Δ_{T-3} .

N_{el}	$\omega = 0.3E_H^*$		$\omega = 1.0E_H^*$	
	2D	3D	2D	3D
3	0.0033	0.0011	0.0028	0.0005
4	0.0097	0.0026	0.0066	0.0014
5	0.0133	0.0046	0.0113	0.0024
6	0.0239	0.0063	0.0153	0.0036
7	0.0237	0.0087	0.0171	0.0052
8	0.0234	0.0114	0.0189	0.0070
10	0.0310	0.0107	0.0226	0.0068
12	0.0424	0.0093	0.0272	0.0064

TABLE VI. Triples correction as percent of correlation energy, $\Delta_{T-3}/\Delta E_{CCSDT-3}$.

N_{el}	$\omega = 0.3E_H^*$		$\omega = 1.0E_H^*$	
	2D	3D	2D	3D
3	2.24%	2.12%	1.41%	0.91%
4	5.55%	3.81%	2.74%	1.66%
5	5.37%	5.15%	3.14%	2.30%
6	6.63%	5.25%	3.29%	2.47%
7	6.91%	5.74%	3.49%	2.76%
8	7.20%	6.35%	3.63%	3.10%
10	7.30%	5.51%	3.83%	2.71%
12	7.49%	4.83%	3.72%	2.50%

For dots with an open-shell ground state, even the lowest excited state can have significant double-excitation character. Consider, for instance, the lowest-lying transition in a 7-electron dot, in which the lone $3d$ electron is excited into the $3s$ level (we ignore the spurious excitation from one $3d$ orbital to the other, as it arises due to lack of cylindrical symmetry in the wave function). At confining frequency $\omega = 0.3E_H^*$, EOM-CCSD predicts an excitation energy of $0.040E_H^*$, but the state has an AEL of 1.28 and the norm of the single-excitation part of the eigenvector is 0.909; clearly, an excited-state method must be able to handle doubly excited states if it is to make accurate predictions of excitation energies and excited-state properties for such a dot. As the confining frequency increases to $\omega = 1E_H^*$, the EOM-CCSD excitation energy rises to $0.074E_H^*$. Here, however, the double-excitation character is much smaller and may no longer be significant; the AEL is 1.08, and the norm of the single-excitation part of the eigenvector is 0.959. While the EOM-CCSD method should be sufficient for this lowest state in the 7-electron dot at this frequency, higher states have larger AEL values and smaller single-excitation parts of the eigenvector, and we thus suspect that some inclusion of triples is probably almost always necessary for dots of this general type (i.e., dots which are one electron removed from a closed shell).

B. Effect of triple excitations

We have seen that many of the excited states for quantum dots, especially for those dots with low confining frequency, have large AEL numbers and correspondingly large double-

excitation character. Hence, some inclusion of triple excitations is expected to be important for the description of excited states. To assess their role, we include triple excitations via the EOM-CCSDT-3 formalism.²² We choose to examine 6- and 12-electron dots. However, it is first worthwhile to assess the effect of triples on the ground state, which can be seen in Tables V and VI.

Inclusion of triples by the CCSDT-3 method²⁹ lowers the ground-state energy by about $0.02E_H^*$ for 6-electron dots and by roughly twice that for 12-electron dots; by molecular standards, these corrections are quite large, as can be seen by noting that the triples corrections in the spherical case (often referred to as Hooke’s atom) are substantially smaller, typically by a factor of 3–4.

However, due to the exceptionally large correlation energy in quantum dots, the importance of triple excitations may be somewhat exaggerated. At the highest frequency examined ($\omega = 1E_H^*$), the triples correction is roughly 4% of the total correlation energy in two dimensions and a somewhat smaller fraction in three dimensions; these numbers are about what is to be expected based on molecular experience. For more weakly confined dots, the relative importance of triples is about twice as large, and triples are evidently important even for the ground state when the confining frequency is small, as is to be expected. For excited states, the EOM-CCSDT-3 triples correction to the excitation energies of singly excited states is fairly small, as can be seen in Table VII. In the 6-electron dot, the effect of triples on representative excited states is only a few mE_H^* ; the situation is similar in the 12-electron dot.

In conclusion, even though the effect of triples on the total energy are large, for both the ground and excited states, the effect of triples on energy differences (such as excitation energies, addition energies, and the like) is surprisingly slight; for lower-lying singly excited states, the excitation energies change only at the mE_H^* level. As the states begin to include more double-excitation character, triples corrections start to grow and will be significant for doubly excited states. At least for the 6-electron dot, it seems likely that triples corrections will be important fairly early in the excitation spectrum, as double-excitation character in the excited-state wave function begins to appear at relatively low excitation energies, while in 12-electron dots the onset of double-excitation character (and hence the need for triples) occurs higher in the excitation spectrum.

TABLE VII. Triples correction to excitation energies for a 6-electron dot.

ω	ϵ_{CCSD}	$\epsilon_{CCSDT-3}$	Dominant excitations	ϵ_{CCSD}	$\epsilon_{CCSDT-3}$	Dominant excitations
0.3	0.089	0.090	$2p \rightarrow 3d / 2p \rightarrow 3s$	0.154	0.151	$2p \rightarrow 3s$
0.4	0.138	0.139	$2p \rightarrow 3d / 2p \rightarrow 3s$	0.223	0.218	$2p \rightarrow 3s$
0.5	0.192	0.193	$2p \rightarrow 3d / 2p \rightarrow 3s$	0.295	0.291	$2p \rightarrow 3s$
0.6	0.249	0.251	$2p \rightarrow 3d / 2p \rightarrow 3s$	0.370	0.367	$2p \rightarrow 3s$
0.7	0.309	0.310	$2p \rightarrow 3d / 2p \rightarrow 3s$	0.446	0.441	$2p \rightarrow 3s$
0.8	0.371	0.372	$2p \rightarrow 3d / 2p \rightarrow 3s$	0.524	0.519	$2p \rightarrow 3s$
1.0	0.499	0.501	$2p \rightarrow 3d / 2p \rightarrow 3s$	0.682	0.678	$2p \rightarrow 3s$

TABLE VIII. Addition energies at two frequencies.

N_{el}	$\omega = 0.5E_H^*$			$\omega = 1.0E_H^*$		
	ΔE_{EOM}	ΔE_{CC+G}	ΔE_{CC}	ΔE_{EOM}	ΔE_{CC+G}	ΔE_{CC}
6	3.157	3.157	3.185 ^a	5.234	5.234	5.259 ^a
7	3.785	3.776	3.782 ^a	6.382	6.375	6.385 ^a
10	5.425	5.425	5.436	8.886	8.887	8.894
12	5.935	5.928	5.959	9.845	9.840	9.886

^aReference 6.

V. IP- AND EA-EOM METHODS

One of the more useful extensions of the standard equation-of-motion formalism is the ability to describe excitation processes in which one electron (or more) is attached or removed from the system, or EA-EOM and IP-EOM, respectively. These allow one to examine excitations in many open-shell systems by starting from a closed-shell wave function, which has the convenient property that the excited-state wave functions are hence pure spin eigenfunctions, which is not the case in standard EOM in an open-shell system. Further, a very important quantity in quantum dot design is the addition spectrum as electrons are added to the dot. One can easily obtain this, the chemical potential, for a closed-shell system with one calculation, rather than requiring separate calculations for the N and $N+1$ electron systems.

Considering first the lowest ionization and electron attachment energies, we calculate the chemical potentials for 6-, 7-, 12-, and 13-electron dots [using EA-EOM for odd electron number and IP-EOM for even electron number: $\mu(N) = E(N) - E(N-1)$]. These results are presented in Table VIII, and comparisons with earlier indirect CCSD energy difference calculations⁶ are made where possible; in other cases, we have made calculations analogous to those of Ref. 6. Note, however, that here we have used the smallest of our basis sets (which includes a pair of g functions and removes some of the lower-angular-momentum functions). Even so, the agreement between the EOM values and the ΔE_{CC} reported previously is generally good. As the number of electrons increases, the effect of g functions on the addition energy becomes more pronounced. This is borne out by ΔE_{CC} calculations in the same basis set as the EOM, also reported in Table VIII as ΔE_{CC+G} .

Because the IP- and EA-EOM methods can give all the ionization potentials or electron affinities, one can also use them to calculate excitation energies in the ionized and electron attached systems, respectively. The EA-EOM results are presented for the 6-electron dot in Table IX for $\omega = 0.3E_H^*$ and $1E_H^*$. Note again that as double excitations become more important, the EOM-CCSD becomes less reliable, and hence only a few excitation energies are presented in each case; once again, we see that double-excitation character becomes substantial for very-low-lying excitations in dots that are one electron removed from a closed shell (note also, however, that the column listed as %SE is the contribution of

TABLE IX. Excitation energies via the EA-EOM method for the 7-electron dot.

$\omega = 0.3E_H^*$		$\omega = 1.0E_H^*$	
ϵ	%SE	ϵ	%SE
0.012	88.5	0.070	94.4
0.145	71.0	0.597	64.1
0.209	77.2	0.789	55.6
0.353	68.5	1.334	51.3

single excitations from the reference 6-electron dot, not the ground state of the 5- or 7-electron dot). Interestingly, even the lowest excited state for the 5-electron dot has substantial double-excitation character. For this, IP-EOM predicts an excitation energy of $0.119E_H^*$ ($0.520E_H^{**}$) and 75.7% single-excitation character (72.5%) at $\omega = 0.3E_H^*$ ($1E_H^*$).

VI. CONCLUSIONS

The EOM-CC formalism provides a convenient way to study excited states of artificial atoms, where correlation can be included without the need for an exact diagonalization of the Hamiltonian. Truncation of the T operator at single and double excitations gives reasonably accurate ground-state energies in an affordable manner, and for excited states dominated by single excitations, the accompanying EOM-CCSD shows accuracy to within a few effective millihartree. Further, the EOM-CCSDT-3 method provides a convenient alternative for states with more double-excitation character, and if need be, full inclusion of triples is possible in EOM-CCSDT.³⁰ By using the IP-EOM and EA-EOM methods, one can study electron attachment or removal processes, so that direct calculation of the addition energy and the lower excitation energies in the electron attached or removed system is possible.

Thus, the CC-EOM framework allows, with an appropriate choice of basis set and appropriate definitions of T , L and R , a highly accurate description of ground and excited states of any sort. There is of course no limitation to a two-dimensional treatment, and in fact the more realistic three-dimensional model is more natural for us. It merely requires the appropriate integrals and basis functions, which in the spherical case are those used in molecular work, although when the dot is not spherical some modifications are necessary. The inclusion of magnetic field effects in these systems can be handled in a similarly straightforward way. These tools all assist in the design of quantum dot devices.

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