Parameter-free shell model of spherical Coulomb crystals

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An accurate shell model of spherical Coulomb crystals is presented. Employing intrashell angular particle positions that correspond to the global energy minima of the pertinent Thomson problems, it yields rigorous upper bounds to the exact energies that are accurate to within 0.03%, which constitutes an improvement of two orders of magnitude over its predecessors based upon continuous intrashell distributions. In addition, the present model faithfully reproduces mean crystal radii and shell occupancies without recourse to any empirical parameters. Thanks to its simple form and the well-known asymptotics of the Thomson problem at the bulk limit, it affords analytical formulas for energies and mean crystal radii of very large spherical Coulomb crystals. Moreover, it rigorously accounts for certain features of the less accurate models published previously.

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I. INTRODUCTION

The concept of spherical Coulomb crystals, i.e., collections of particles interacting through a sum of Coulombic and harmonic potentials [1], emerges in diverse branches of physics and chemistry. In plasma research, it is employed in the description of low-temperature gases of ions confined by electromagnetic traps [2,3] and in studies of dusty plasmas [4]. In the solid state, two-dimensional Coulomb crystals are known as Wigner molecules (quantum dots at low confinement strengths) [5]. In the electronic structure theories of quantum chemistry, they constitute the strong-correlation limits of harmonium atoms that are used in calibration and benchmarking of approximate approaches to the electron correlation problem [6], making the knowledge of their properties a prerequisite for derivation of the relevant electronic wave functions [7,8].

The particle configurations that correspond to the global minima of the potential energy

$$E(N) = \sum_{i>j=1}^{N} \epsilon(r_{ij}), \tag{1}$$

where

$$\epsilon(r) = \frac{1}{3}\,(r^2 + 2r^{-1}), \tag{2}$$

exhibit well-pronounced shell structures [9–11]. In this paper, we present a simple formalism that, by faithfully modeling this feature, yields very accurate property estimates for spherical Coulomb crystals.

II. THEORY

Consider K concentric spherical shells with the radii $\{R_k\}$ (where $\forall_k\ R_{k+1} > R_k$) and occupancies $\{n_k\}$ that satisfy the condition

$$\sum_{k=1}^{K} n_k = N. \tag{3}$$

The angular particle positions within the kth shell are those of the global energy minimum $E_{Th}(n_k)$ of the Thomson problem (i.e., n_k electrons confined to the surface of a sphere with a unit radius [12,13]). The intershell interactions are approximated by the first (monopole-monopole) term of the pertinent multipole expansion. Under the assumption

$$\sum_{i=1}^{N} \vec{r}_i = 0, \tag{4}$$

the potential energy $E(N)$ of a spherical Coulomb crystal of N particles is thus

$$E(N) \approx \min_{\{R_k\}} \min_{\{n_k\}} \left\{ \frac{2}{3} \sum_{k=1}^{K} n_k \left[\frac{1}{2}\nu(n_k) + \sum_{l=1}^{k-1} n_l \right] R_k^{-1} + \frac{N}{3} \sum_{k=1}^{K} n_k R_k^2 \right\}, \tag{5}$$

which upon minimization with respect to $\{R_k\}$ produces

$$R_k = N^{-1/3} \left[\frac{1}{2}\nu(n_k) + \sum_{l=1}^{k-1} n_l \right]^{1/3}, \tag{6}$$

where

$$\nu(n) = \frac{2}{n}\, E_{Th}(n). \tag{7}$$

Therefore,

$$E(N) \approx \min_{\{n_k\}} \left\{ N^{1/3} \sum_{k=1}^{K} n_k \left[\frac{1}{2}\nu(n_k) + \sum_{l=1}^{k-1} n_l \right]^{2/3} \right\}, \tag{8}$$

and

$$\langle r_i \rangle(N) \approx N^{-1} \sum_{k=1}^{K} n_k R_k = N^{-4/3} \sum_{k=1}^{K} n_k \left[\frac{1}{2}\nu(n_k) + \sum_{l=1}^{k-1} n_l \right]^{1/3}. \tag{9}$$

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Shell models of spherical Coulomb crystals involving continuous surface charge distributions that give rise to spherical capacitors have been considered in the past [14–16]. Hasse and Avilov (HA) proposed a model with $\nu(n)=n$ [14], whereas Tsuruta and Ichimaru (TI) set $\nu(n)=n-n^{1/2}$ together with additional correction terms [15]. There has also been a recent attempt by Kraeft and Bonitz (KB) to improve the poor performance of the HA and TI approximations by introducing an empirical correction factor $\tau \approx 1.104$ in $\nu(n)=n-\tau n^{1/2}$ [16]. It should also be noted that a model analogous to the present one has been considered for the much simpler two-dimensional case, where the particles are located at the vertices of regular polygons sharing a common center [17].

Despite the appearance of being a minor modification, the present model constitutes a dramatic improvement over the HA, TI, and KB approaches. First of all, as reflected by the maximum relative error of 0.03% compared with that of 5% reported for the TI model [16] it produces energy estimates that are orders of magnitude more accurate than those afforded by its predecessors. Second, it does not rely on any empirical parameters. Third, even more importantly, as the neglect of the higher-order terms in the multipole expansion is equivalent to averaging the energy over $3K$ Euler angles describing the shell rotations, the right-hand side of the expression (8) is greater or equal to the actual sum of the intra- and intershell energies, which in turn is greater or equal to the exact energy of spherical Coulomb crystal that obtains upon further relaxation of the particle positions. Consequently, the expression (8) provides an extremely accurate, rigorous upper bond to the exact energy. Fourth, as the conjectured large-n behavior of the Thomson energy [18,19] yields

$$\nu(n) = n - \xi_1 n^{1/2} + \xi_2 n^{-1/2} + \cdots \tag{10}$$

(note the appearance of a term that explains the observed improvement in the performance of the KB model over its TI counterpart), the present approach readily lends itself to an analytical workout that results in the large-N asymptotics

$$e(N) = \frac{6}{5}\left[1 - \frac{5}{4}\left(\frac{\xi_1^4}{3}\right)^{1/3} N^{-2/3}\right] + \cdots, \tag{11}$$

and

$$\langle r_i \rangle(N) = \frac{3}{4}\left[1 - \frac{1}{2}\left(\frac{\xi_1^4}{3}\right)^{1/3} N^{-2/3}\right] + \cdots \tag{12}$$

for the energy $e(N)=2[N(N-1)]^{-1}E(N)$ per particle pair and the mean crystal radius $\langle r_i \rangle(n)$ [see the text following Eq. (14) for the explanation of the origin of these expressions].

Results of test calculations employing the published values of $E_{Th}(n)$ for all $n<400$ [13] testify to the predictive power of the present model. For spherical Coulomb crystals of up to 160 particles, for which results of reliable searches for the global energy minima are known [9–11], the values of $e(N)$ are reproduced within 3.2×10^{-4} [note that the inequality $\forall_N\ 1 \leqslant e(N) \leqslant \frac{6}{5}$ holds, hence the absolute and relative errors are essentially the same], with the largest error attained at $N=29$ in the case of shell occupancies taken from the literature data (Fig. 1). The error in $e(N)$ diminishes only slightly (to the maximum value of 3.1×10^{-4} for $N=27$) upon optimization of the shell occupancies $\{n_k\}$. In all cases, the upper-boundedness property is observed, as expected. Interestingly, the predicted mean crystal radii $\langle r_i \rangle(N)$ are always either exact or underestimated (by at most 7×10^{-4} for $N=29$) when the fixed occupancies are used (Fig. 2). Although optimizing the shell occupancies worsens the accuracy significantly, the relative error in $\langle r_i \rangle(N)$ remains below 0.5%. The optimized shell occupancies faithfully reproduce their actual counterparts (Fig. 3). In fact, among spherical Coulomb crystals of up to 160 particles, correct shell occupancies are predicted in 110 instances, the remaining 50 cases arising from 39 single and 11 double particle misassignments.

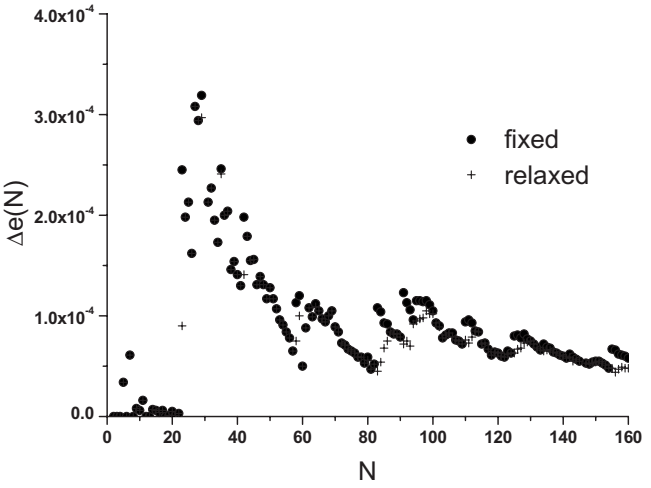

FIG. 1. Errors in the energies per particle pair computed with fixed (i.e., the exact ones) and relaxed [i.e., those resulting from minimization of the approximate energy expression (8)] shell occupancies vs the number of particles.

The published values of $E_{Th}(n)$ [13] suffice for treatment of spherical Coulomb crystals of up to approximately 1000

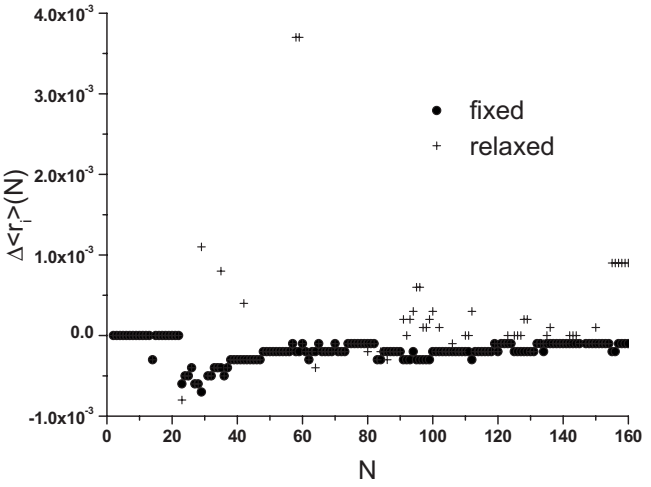

FIG. 2. Errors in the mean crystal radii computed with fixed (i.e., the exact ones) and relaxed [i.e., those resulting from minimization of the approximate energy expression (8)] shell occupancies vs the number of particles.

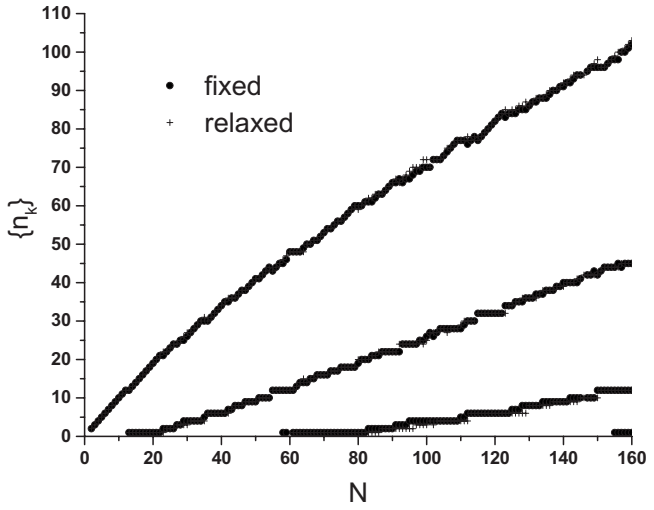

FIG. 3. The predicted and actual shell occupancies vs the number of particles.

particles. The scarcity of solutions of the Thomson problem beyond 400 electrons does not hinder the usefulness of the present model, as the asymptotic formula (10) with $\xi_1=1.105\,02$ and $\xi_2=0.253\,108$ [20] accurately reproduces the available data for $n>400$. One should note that the fitted value of ξ_1 is close to that of 1.104 60 quoted previously [19] and not far from the upper bound (and in fact the conjectured exact value [18]) of

$$\frac{3^{3/4}}{\sqrt{2\pi}}\left[\zeta\left(\frac{1}{2},\frac{2}{3}\right)-\zeta\left(\frac{1}{2},\frac{1}{3}\right)\right]\zeta\left(\frac{1}{2},0\right)\approx 1.106\,10, \quad (13)$$

where $\zeta(s,a)$ is the generalized Riemann zeta function. Needless to say, the present model accounts for the magnitude of the empirical correction τ employed in the KB approach [16].

The predicted shell capacities (i.e., the maximum shell occupancies) $\{m_k\}$ together with properties of the spherical Coulomb crystals with the corresponding total numbers of particles $\{M_k\}$ are displayed in Table I. The present model correctly predicts the first two shell capacities of 12 and 48. However, the expected appearances of the third and fourth shells lag behind the observed ones. In particular, the third shell is predicted to emerge for $N=61$, whereas it is already found in the crystals of 58 and 59 particles [9–11]. Similarly, although the crystals of 155–160 particles are already composed of four shells, the model predicts this to occur only for $N>164$. Interestingly, these discrepancies are not caused by incorrect values of $\{m_k\}$ but by the fact that the crystals tend to acquire new shells before capacities of the existing ones are exhausted (note that the crystal of 60 particles is composed of two shells with occupancies of 12 and 48, as predicted).

The large-k asymptotics of the shell capacities, given by

$$m_k=9\xi_1^2\,k^2\approx 10.9896\,k^2, \quad (14)$$

is obtained by comparing the energies of the spherical Coulomb crystals with the shell occupancies of $\{1,m_1,\ldots,m_k\}$ and $\{m_1,\ldots,m_k+1\}$, which yields

TABLE I. The predicted shell capacities, and the corresponding total number of particles, energies per particle pair, and mean crystal radii.

k	m_k	M_k	$e(M_k)$	$<r_i>(M_k)$
1	12	12	1.06582	0.6989
2	48	60	1.14209	0.7317
3	104	164	1.16764	0.7404
4	182	346	1.17937	0.7441
5	282	628	1.18572	0.7460
6	409	1037	1.18957	0.7471
7	555	1592	1.19205	0.7478
8	723	2315	1.19373	0.7483
9	912	3227	1.19493	0.7486
10	1124	4351	1.19582	0.7489
11	1358	5709	1.19649	0.7491
12	1613	7322	1.19701	0.7492
13	1891	9213	1.19743	0.7493
14	2191	11404	1.19776	0.7494
15	2512	13916	1.19803	0.7495
16	2856	16772	1.19826	0.7495
17	3221	19993	1.19845	0.7496
18	3609	23602	1.19861	0.7496
19	4018	27620	1.19874	0.7497

$$\sum_{k=1}^{K} m_k\left[\frac{1}{2}\nu(m_k)+M_{k-1}+1\right]^{2/3} - \sum_{k=1}^{K}(m_k+\delta_{kK})\left[\frac{1}{2}\nu(m_k+\delta_{kK})+M_{k-1}\right]^{2/3}=0. \quad (15)$$

Subtraction of the above conditions for K and $K+1$ reveals that their compatibility with the first two terms of the asymptotic expression (10) calls for

$$m_k=A\,k^2+\cdots, \quad (16)$$

where A satisfies the equation

$$(\sqrt{A}-3\xi_1)\,3^{-5/3}A^{1/6}\left(-K^{-1}+\frac{1}{2}K^{-2}+\cdots\right)=0, \quad (17)$$

from which Eq. (14) follows immediately. Substitution of this result into the approximations (8) and (9) produces the asymptotics (11) and (12) after some tedious algebra. The numerical value of the proportionality constant in Eq. (14) explains the previously observed [14] (and as it now turns purely accidental) similarities between the shell capacities and the magic Mackay icosahedra numbers.

III. DISCUSSION AND CONCLUSIONS

In summary, the shell model presented in this paper relates in an approximate fashion properties of spherical Coulomb crystals to the solutions of the Thomson problem. The

accuracy of the resulting predictions is impressively high in light of the neglect of both the particle-position relaxation and the higher multipole moments of individual shells, though the latter deficiency is obviously mitigated by the small magnitudes of these moments for the shells with large occupancies that contribute the most to the total energy.

In principle, inclusion of higher multipole interactions, coupled with optimization of the Euler angles describing relative shell orientations, could be carried out. One doubts, however, whether the resulting marginal gains in accuracy would justify sacrificing the elegant simplicity of the present approach.

[1] The potential energy $E=\Sigma_{i>j=1}^{N} r_{ij}^{-1}+(\omega^2/2)\Sigma_{i=1}^{N} r_i^2$ of N harmonically confined particles is conveniently rewritten as $E=\Sigma_{i>j=1}^{N}[r_{ij}^{-1}+(\omega^2/2N)\, r_{ij}^2]+(N\omega^2/2)R_{CM}^2$, where $\vec{R}_{CM}$ is the center-of-mass position. Upon scaling the interparticle distances and the energy by $(N/\omega^2)^{1/3}$ and $(3/2)(\omega^2/N)^{1/3}$, respectively, Eqs. (1) and (2) follow upon the assumption given by Eq. (4). Such a dimensionless formulation has the advantage of being translationally invariant, allowing for the application of several theoretical techniques developed for other clusters with pairwise double-power-law interactions (such as the Lennard-Jones ones).

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