Electronic Supplementary Information : Widening of the Fundamental Gap in Cluster *GW* for Metal-Molecular Interfaces

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1 Clustering of Pyramidal Energy Levels

Pyramidal clusters contain approximate symmetries that cause pairing/clustering of energy levels together. This clustering is shown in Fig. 1.

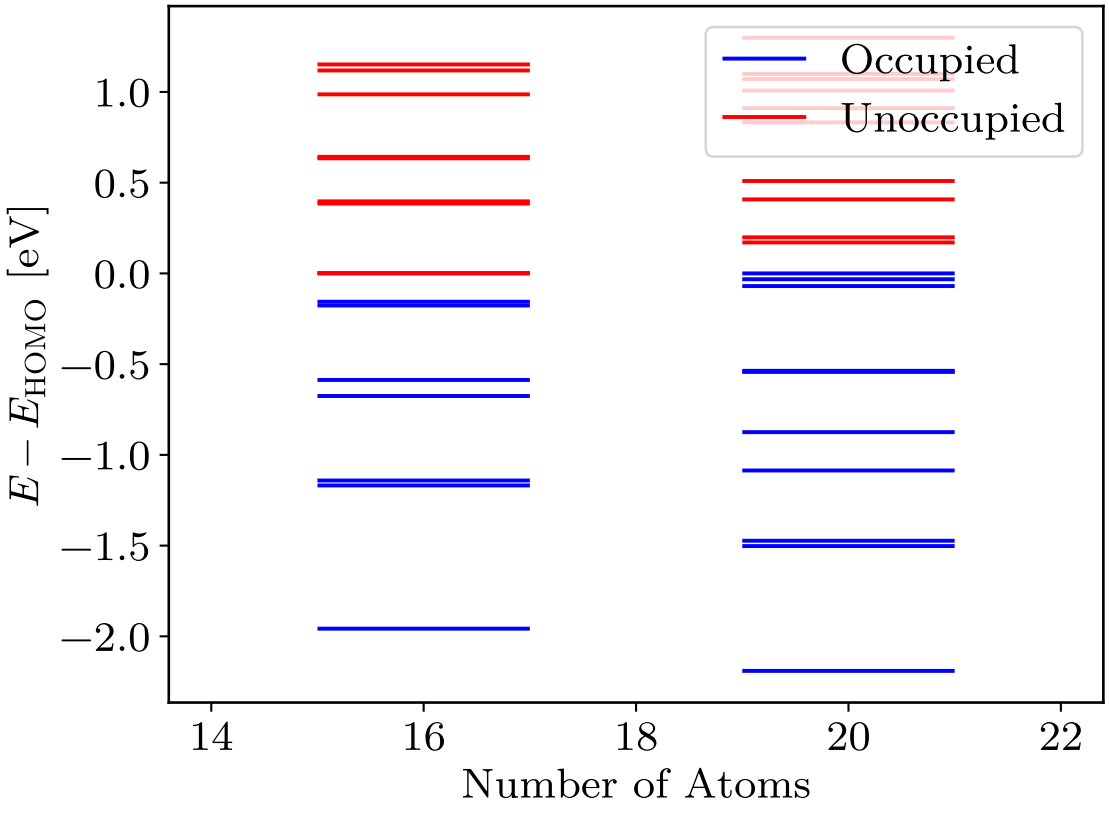

Figure 1: Positions of energy levels for pyramidal clusters (see Fig. 6 in main text) in DFT. Notice that levels tend to form near-degenerate pairs, or cluster in groups. This greatly increases the error in statistical treatment of the spectral gaps.

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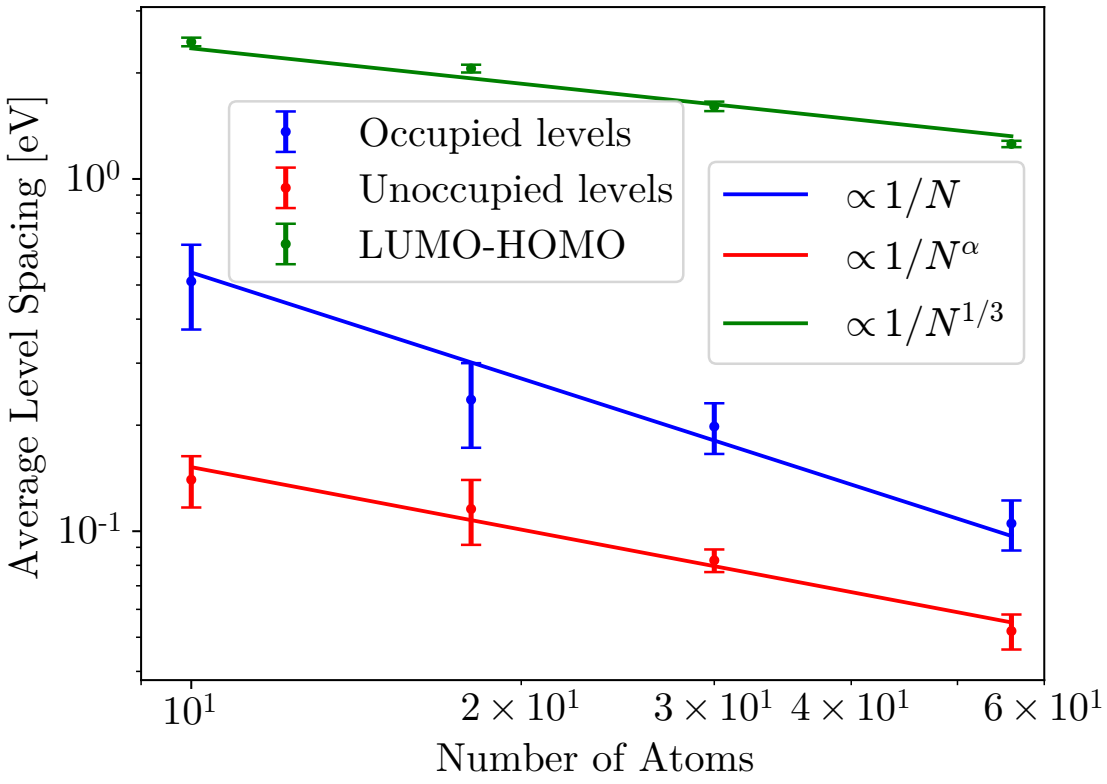

Figure 2: The average LUMO-HOMO gap and energy level spacings in $G0W0$ method. This method is less computationally demanding, and hence even results for larger clusters than in evGW are present. The dependency of gap and orbital spacings remains the same as in the evGW case, although the values of the gap itself are smaller.

2 Electronic Structure Indicators in $G0W0$

While evGW provides advantages such as reduced starting functional dependence, it is known to have more pronounced errors due to missing vertex corrections, which is a deficiency of the entire GW scheme[1]. The missing consistency in single shot $G0W0$ in at least some cases causes underestimation of the gap, which leads to more accurate results.

We calculated the gaps and level spacings in $G0W0$ as well and investigated the behaviour in the same way as in main text, as presented in Fig. 2. It is clear that the $N^{-1/3}$ behaviour is also present in the $G0W0$ formalism.

3 Basis Convergence

In order to make predictions based on the electronic structure calculations, convergence with respect to basis size has to be achieved. In figures below, we present some of the calculations done in main text in larger basis set def2-TZVP. In all cases, the results in this larger basis are compatible with results from smaller basis. In some cases, specific values are different, but overall trends such as scaling with number of atoms remain same as in the smaller basis. Therefore, it is deemed sufficient to address results from def2-SVP only in main text.

The convergence of DFT calculations with respect to basis set size is displayed in Fig. 3. Same convergence but for HF calculations is presented in Fig. 4. For evGW, the basis set size convergence is presented in Fig. 5

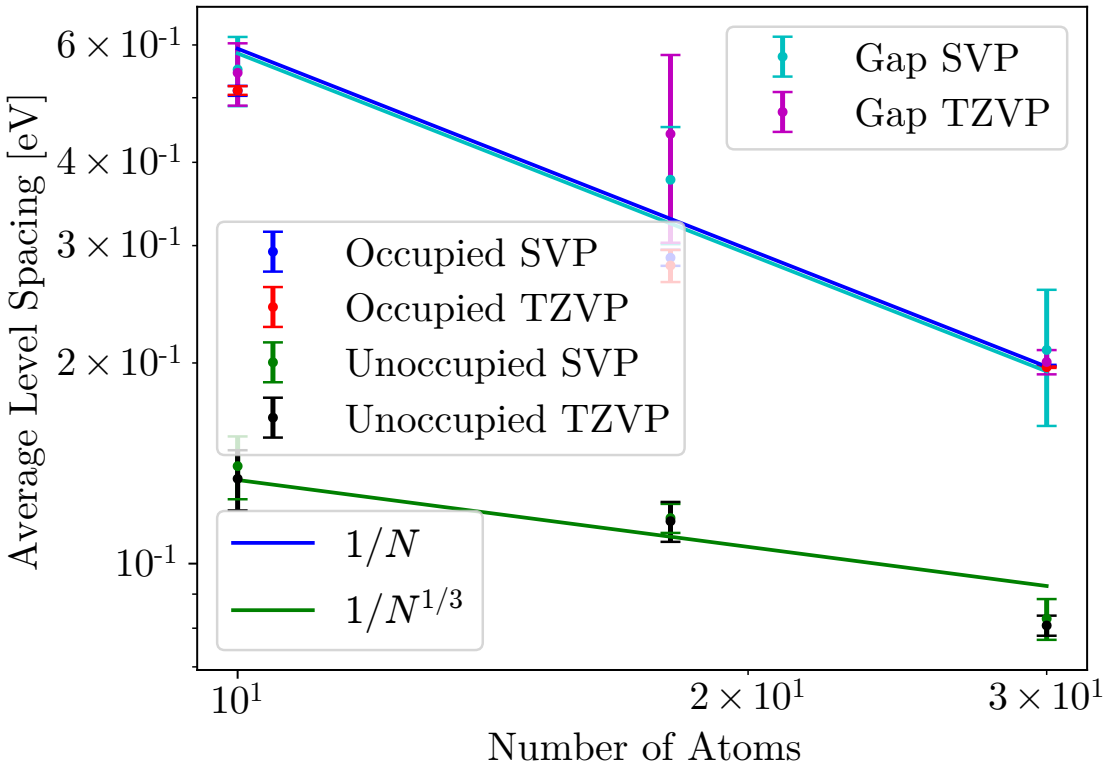

Figure 3: Gap and average energy level convergence of DFT calculations with respect to basis size. For unoccupied levels and gap, the results are compatible. For occupied levels, values of energy spacing are slightly lower, but the trend that can be deduced from the increase of cluster size remains unaffected by the basis size.

4 Functional Dependence

It is reasonable to investigate whether the observed variables are not a peculiarity of the DFT functional used in the calculations. To verify the robustness of the observed trends with respect to functional change, some of the DFT and evGW calculations were repeated with PWLDA functional[2]. The DFT properties are shown in Fig. 6, the evGW properties in Fig. 7. Other parameters of the calculations are same as in the main text.

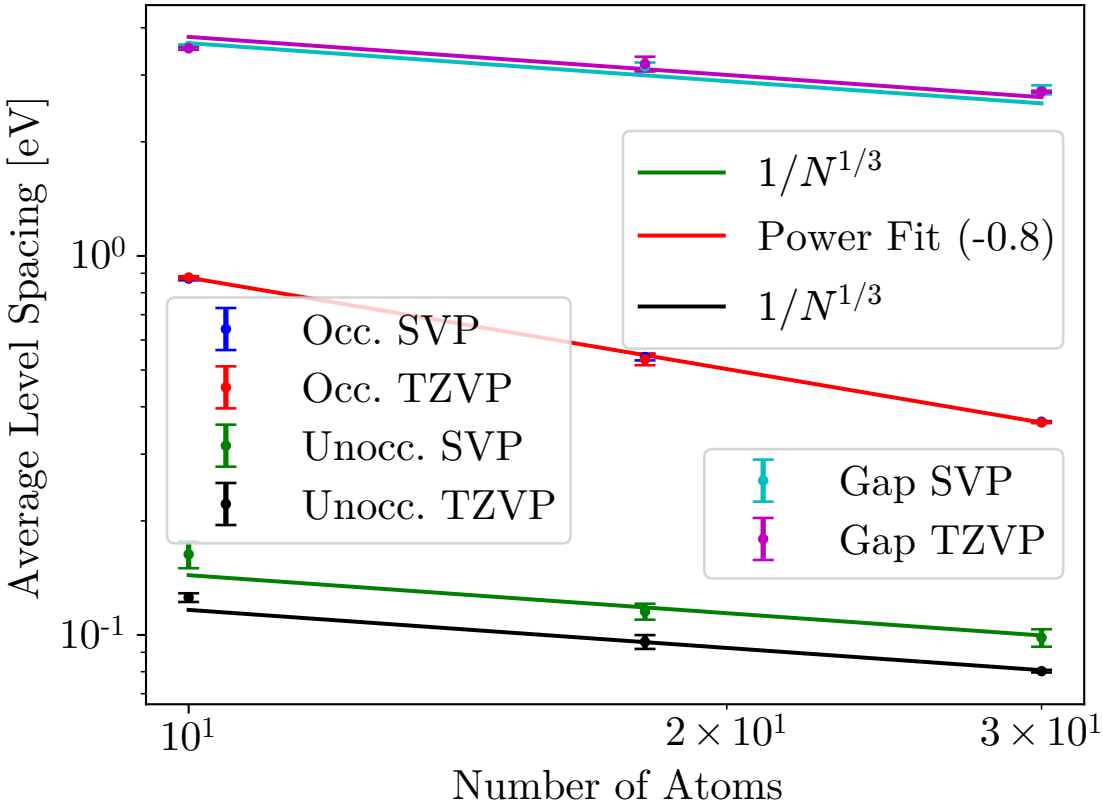

Figure 4: Gap and energy level convergence of HF calculations with respect to basis size. Gap and occupied levels trends that can be deduced from the number of atoms remain unaffected by the increase of the basis set size - unoccupied level spacing is decreased in larger basis, but the scaling remains consistent.

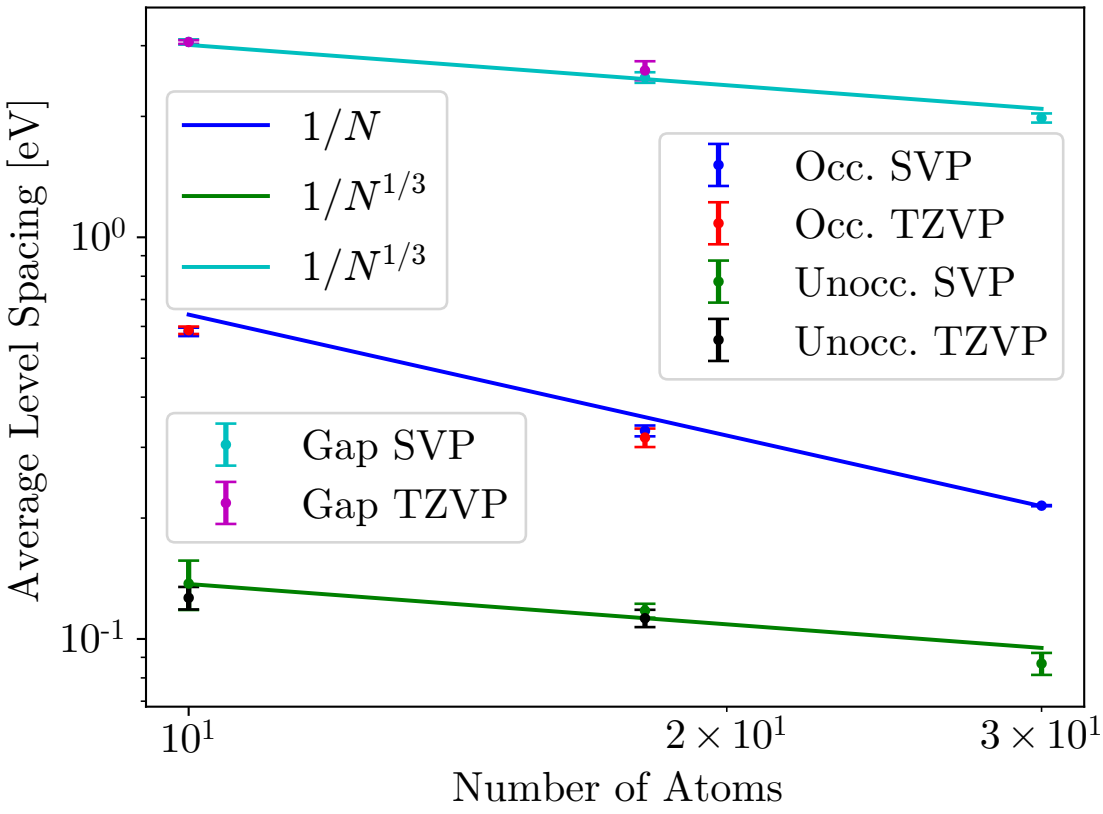

Figure 5: Gap and energy level convergence of evGW calculations with respect to basis size. Already for 30 atoms, the cost of full evGW calculation with larger (TZVP) basis is prohibitively expensive in our current approach. Within the few points for smaller cluster realisations, trends are fully consistent across the different basis set sizes.

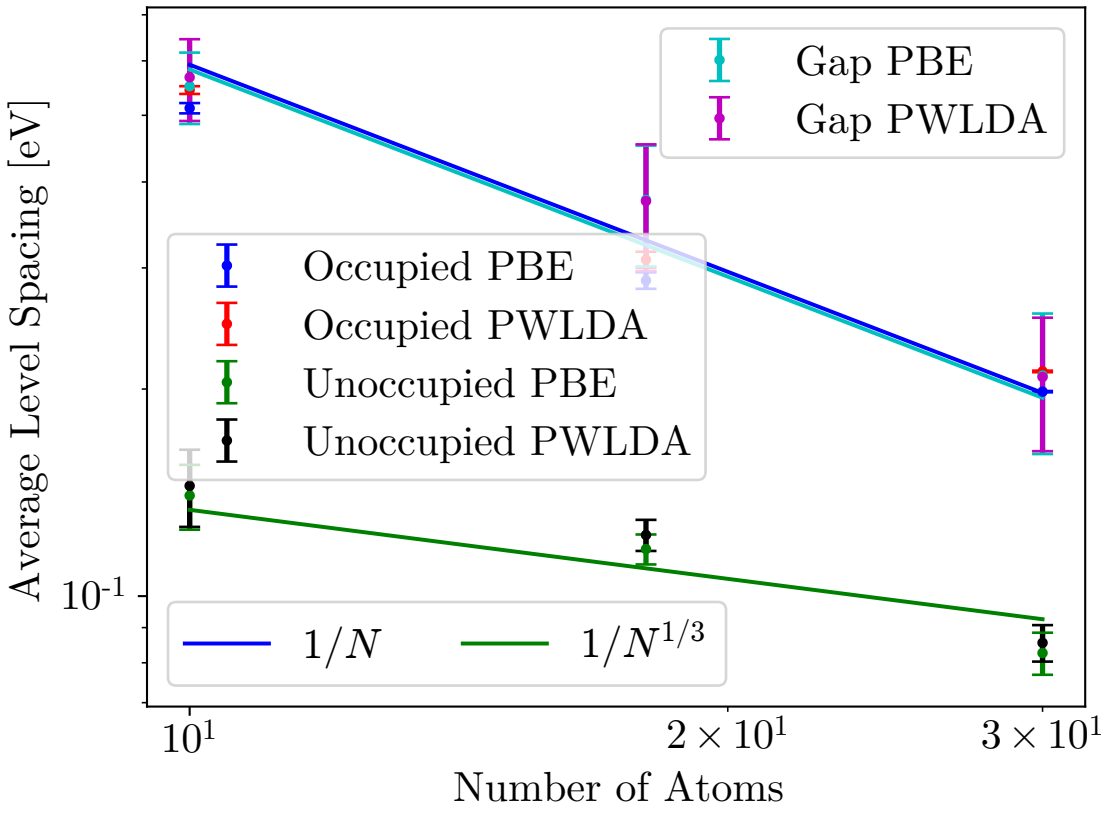

Figure 6: Gap and average energetic spacings in DFT for different functionals used. While there are small numerical differences, overall trends are robust under functional exchange.

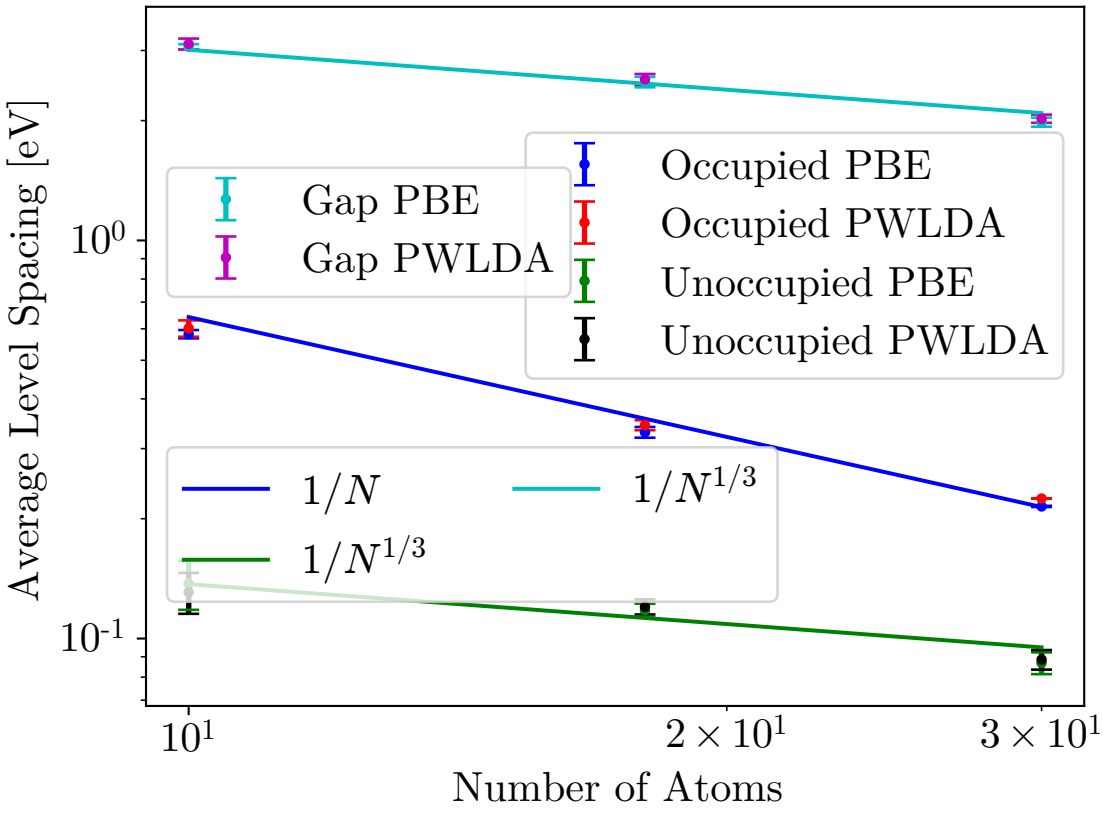

Figure 7: Gap and average spacing values in evGW for different functionals used in the initial DFT calculation. The differences between results for different functionals are even smaller than in the pure DFT case, thanks to the partial self-consistency achieved in evGW (restricted to eigenvalues, not orbitals).

5 Energy of a Homogeneously Charged Sphere

To gain insight into the scaling of charging energies of metallic clusters, we turn to simple electrostatic models. Assuming a uniform charge distribution $\rho(\vec{r}) = \frac{-e}{V}$ on a sphere of volume V (and radius R), the electrostatic energy of repulsion is given as

$$U = \int d^3r_1 \int d^3r_2 \frac{e^2}{4\pi\epsilon_0 V^2 |\vec{r}_1 - \vec{r}_2|} = \frac{e^2}{4\pi\epsilon_0 V^2} \int d^3r_1 \int d^3r_2 \frac{1}{|\vec{r}_1 - \vec{r}_2|}. \tag{1}$$

Using spherical coordinates (r_2, θ_2, ϕ_2) with axis along $\vec{r}_1$ for the inner integration, we have

$$\int d^3r_2 \frac{1}{|\vec{r}_1 - \vec{r}_2|} = \int_0^3 r_2^2 dr_2 \int_{-1}^1 d(\cos\theta_2) \int d\phi_2 \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}}. \tag{2}$$

Integrating with respect to $\cos\theta_2$ and ϕ_2 leads to

$$\int_0^R r_2^2 dr_2 2\pi \left[\frac{1}{r_1 r_2} \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 z} \right]_1^{-1} = 2\pi \int_0^R \frac{r_2}{r_1} dr_2 \left(r_1 + r_2 - |r_1 - r_2| \right). \tag{3}$$

Substituting into the outer integral and integrating the angular coordinates as well leads to

$$U = \frac{2e^2\pi}{\epsilon_0 V^2} \int_0^R \int_0^R r_1 dr_1 r_2 dr_2 (r_1 + r_2 - |r_1 - r_2|). \tag{4}$$

We split the inner integral into two parts

$$U = \frac{2e^2\pi}{\epsilon_0 V^2} \int_0^R r_1 dr_1 \left(\int_0^{r_1} dr_2 r_2 (r_1 + r_2 - r_1 + r_2) + \int_{r_1}^R dr_2 r_2 (r_1 + r_2 - r_2 + r_1). \right) \tag{5}$$

Integrating by r_2 leads to

$$U = \frac{2e^2\pi}{\epsilon_0 V^2} \int_0^R r_1 dr_1 \left(\frac{2}{3} r_1^3 + r_1 \left(R^2 - r_1^2 \right) \right) = \frac{2e^2\pi}{\epsilon_0 V^2} \left(\frac{2}{15} + \frac{1}{3} - \frac{1}{5} \right) R^5 . \tag{6}$$

Hence,

$$U = \frac{2e^2}{\epsilon_0 V^2} \left(\frac{R^2}{5} \right) \left(\frac{4}{3}\pi R^3 \right) \propto \frac{1}{V^{\frac{1}{3}}} \propto \frac{1}{N^{\frac{1}{3}}} \tag{7}$$

6 Energy of a Screened Charge on a Sphere

We can similarly integrate the uniformly distributed charge with the shielded Yukawa potential instead of the bare Coulomb potential. We have

$$U = \frac{e^2}{4\pi\epsilon_0 V^2} \int d^3r_1 \int d^3r_2 \frac{e^{-|\vec{r}_1 - \vec{r}_2|/L_s}}{|\vec{r}_1 - \vec{r}_2|} \tag{8}$$

Again, we define spherical polar coordinates with z-axis pointing along the direction of $\vec{r}_1$, then

$$U = \frac{e^2}{2\epsilon_0 V^2} \int d^3r_1 \int_0^R r_2^2 dr_2 \int_{-1}^1 dz \frac{e^{-\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 z}/L_S}}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 z}} \tag{9}$$

The internal integral can be exactly evaluated

$$\int_{-1}^1 dz \frac{e^{-\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 z}/L_S}}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 z}} = \left[\frac{L_S}{r_1 r_2} e^{-\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 z}/L_S} \right]_{-1}^1 = \tag{10}$$

$$= \frac{L_S}{r_1 r_2} \left(e^{-|r_1 - r_2|/L_S} - e^{-(r_1 + r_2)/L_S} \right) \tag{11}$$

Carrying out the integration with respect to angular directions in the outer integral leads to

$$U = \frac{2\pi e^2 L_S}{\epsilon_0 V^2} \int_0^R r_1 dr_1 \int_0^R r_2 dr_2 \left(e^{-|r_1 - r_2|/L_S} - e^{-(r_1+r_2)/L_S} \right) \tag{12}$$

For the first term, we again split the integration range so that we account for the change of sign in absolute value. The second term can be integrated directly

$$\int_0^R r_1 e^{-r_1/L_S} dr_1 \int_0^R r_2 e^{-r_2/L_S} dr_2 = L_S^4 \left(1 - \left(\frac{R}{L_S} + 1 \right) e^{-R/L_S} \right)^2 \tag{13}$$

The first term is split as

$$\int_0^R r_1 dr_1 \left[\int_0^{r_1} dr_2 r_2 e^{-r_1/L_S} e^{r_2/L_S} + \int_{r_1}^R dr_2 r_2 e^{r_1/L_S} e^{-r_2/L_S} \right] \tag{14}$$

These can be again integrated

$$\int_0^{r_1} dr_2 r_2 e^{r_2/L_S} = L_S^2 \left(\left(\frac{r_1}{L_S} - 1 \right) e^{r_1/L_S} + 1 \right) \tag{15}$$

$$\int_{r_1}^R dr_2 r_2 e^{-r_2/L_S} = L_S^2 \left(\left(\frac{r_1}{L_S} + 1 \right) e^{-r_1/L_S} - \left(\frac{R}{L_S} + 1 \right) e^{-R/L_S} \right) \tag{16}$$

Hence, we have six separate terms as follows (marked as I_n)

$$I_1 = \int_0^R dr_1 r_1 e^{-r_1/L_S} L_S r_1 e^{r_1/L_S} = L_S \int_0^R dr_1 r_1^2 = \frac{1}{3} L_S^4 \frac{R^3}{L_S^3} \tag{17}$$

$$I_2 = \int_0^R dr_1 r_1 e^{-r_1/L_S} (-L_S^2) e^{r_1/L_S} = -\frac{1}{2} L_S^4 \frac{R^2}{L_S^2} \tag{18}$$

$$I_3 = \int_0^R dr_1 r_1 e^{-r_1/L_S} L_S^2 = L_S^4 \left(1 - \left(\frac{R}{L_S} + 1 \right) e^{-R/L_S} \right) \tag{19}$$

$$I_4 = \int_0^R dr_1 r_1 e^{r_1/L_S} L_S r_1 e^{-r_1/L_S} = \frac{1}{3} L_S^4 \frac{R^3}{L_S^3} \tag{20}$$

$$I_5 = \int_0^R dr_1 r_1 e^{r_1/L_S} L_S^2 e^{-r_1/L_S} = \frac{1}{2} L_S^4 \frac{R^2}{L_S^2} \tag{21}$$

$$I_6 = \int_0^R dr_1 r_1 e^{r_1/L_S} (-L_S^2) \left(\frac{R}{L_S} + 1 \right) e^{-R/L_S} = \tag{22}$$

$$= -L_S^4 \left(\frac{R}{L_S} + 1 \right) e^{-R/L_S} \left(\left(\frac{R}{L_S} - 1 \right) e^{R/L_S} + 1 \right) = \tag{23}$$

$$= -L_S^4 \left(\left(\frac{R^2}{L_S^2} - 1 \right) + \left(\frac{R}{L_S} + 1 \right) e^{-R/L_S} \right) \tag{24}$$

Summing together all the terms, we obtain

$$U = \frac{2\pi e^2}{\epsilon_0 V^2} L_S^5 \left[1 - \frac{R^2}{L_S^2} + \frac{2}{3} \frac{R^3}{L_S^3} - \left(\frac{R}{L_S} + 1 \right)^2 e^{-2R/L_S} \right] \tag{25}$$

It can be checked (by Taylor expansion of the exponential) that for $R/L_S \to 0$ (no screening) we recover expression (7). On the other hand, in the case of large cluster, we expect $R/L_S \gg 1$. In that case, the cubic term dominates the expression and we have

$$U \approx \frac{e^2}{\epsilon_0 V^2} L_S^2 \left(\frac{4}{3} \pi R^3 \right) \propto \frac{1}{V} \tag{26}$$

7 Coordinate Files

Ensembles of different clusters were used to get average gaps and energy spacings. The coordinate files of chosen clusters (those without random degeneracies) in the XYZ format are presented below, ordered by number of atoms. These were generated by

1. Taking a subset of sodium bulk (BCC) crystal that fits within a sphere of certain radius
2. Introducing additional atoms at lattice sites neighbouring the sites chosen in first step
3. Relaxing the resulting structure in DFT, using PBE functional, def2-SVP/TZVP basis and converging the energy change between relaxation iterations to less than 10^{-6} a.u.

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7.1 Discarded Clusters

For reference, we also provide clusters which showed random degeneracies

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