DNA base pair and Nano-DNA interactions

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Parameter free consistent-exchange van der Waals density functional

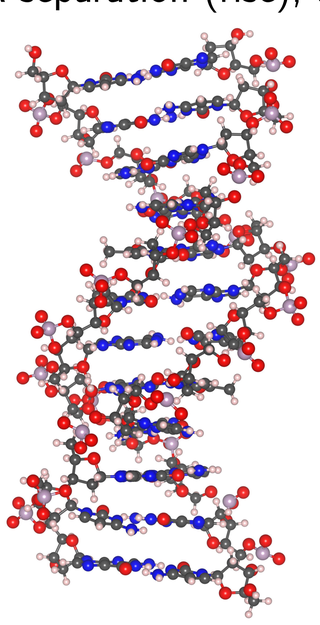
The van der Waals density functional (vdW-DF) method is a non empirical approach to compute the exchange and correlation energy for efficient first-principle theory calculations. Our recent consistent-exchange formulation vdW-DF-cx [1] uses the Dyson equation to balance the truly nonlocal component $E_{\rm c}^{\rm nl}$ with a specially designed gradient-corrected exchange choice $E_{\rm x}^{\rm cx}$ in the functional specification [2]

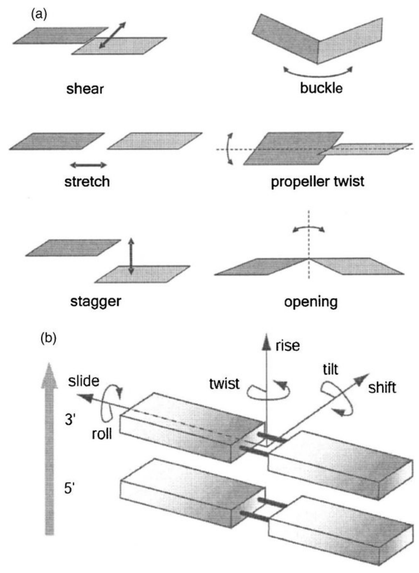
$$E_{\rm xc}^{\rm DF-cx} = E_{\rm x}^{\rm cx} + E_{\rm xc}^{\rm LDA} + E_{\rm c}^{\rm nl} .$$

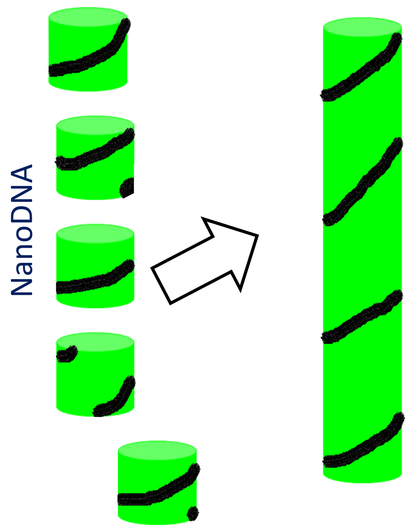
We trust the non empirical vdW-DF-cx as a general-purpose materials theory, it performs better than constraint-based GGAs for thermophysical properties [3] and surface energies/workfunctions [2] of transitions metals, accurately for molecular interactions [4, 2], and has an unprecedented accuracy for describing intermolecular vibrations in organic/polymer crystals [4, 5].

Biochemistry-lego model of base-pair organization in DNA

Experimental data from crystalline DNA has been used to understand the biochemistry model of the base pair organization. The interaction within the structure can be defined by the competition between the vdW interaction, steric hindrance and other forces in between the base pairs. These can be understood by stacking of the base pairs as described by the rise, twist, roll, and slide of the elementary unit. On the other hand, DNA also contains a backbone, including phosphate linker units; the backbone correlates with average structural parameters of stacking of DNA. NanoDNA contains only a few base pairs, and the backbone is short. The base pairs in DNA are typically lying flat and parallel, and with a 3 Å separation (rise), a size that reveals a key importance of the vdW attraction.







vdW-DF-cx implementation

The vdW-DF-cx has excellent scaling even to biochemistry scale (10^6 atoms), e.g., by launching our library LIBVDWXC [6].

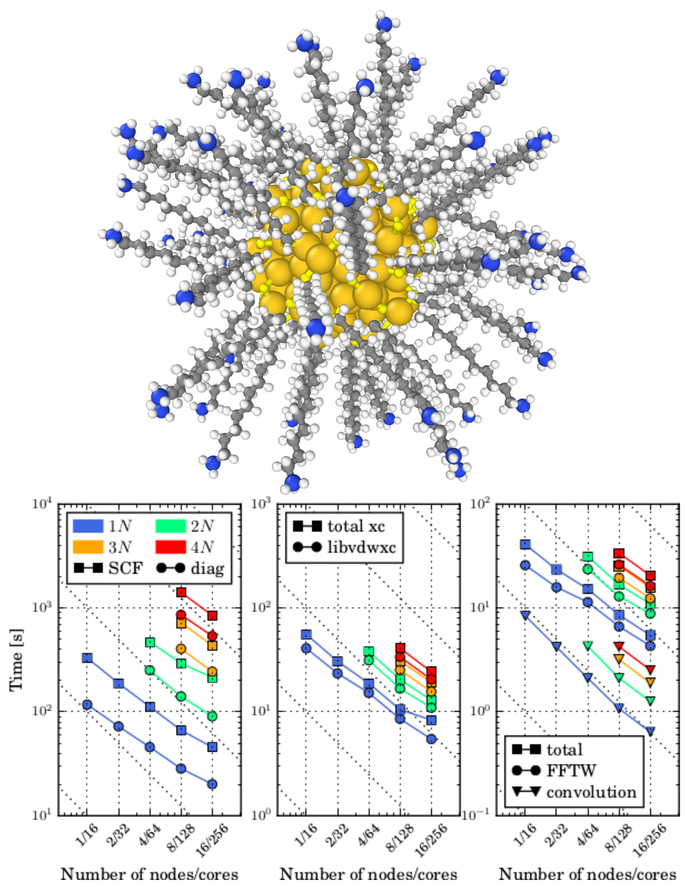


Figure 1: *Linear vdW-DF-cx scaling, via libvdwxc. Scaling for organics-coated gold nano-particles (2500-10000 atoms).*

Base pair interactions

Stacking interactions between the base pairs are important for defining the twist angle and rise. vdW interactions[1] dominate in the stacking of base pairs. The spatially resolved binding contribution $\Delta e_{\rm c}^{\rm nl}(\vec{r})$, defined by the vdW-DF-cx nonlocal-correlation energy term $E_{\rm c}^{\rm nl}[n]$, enhance with parallel geometries.

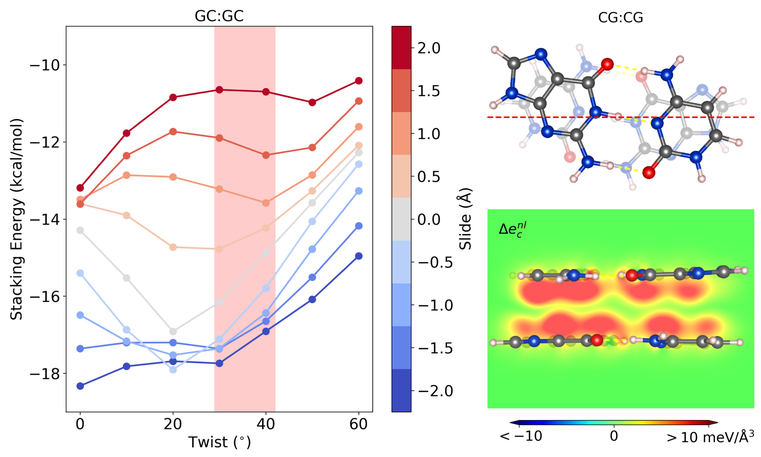
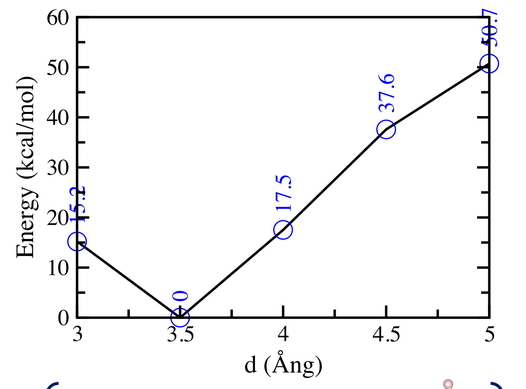


Figure 2: *Stacking energy of two guanine-cytosine base pairs (GC:GC), without backbone. Shaded region shows the energetically favorable stacking twist in experimental results. Highly planar geometries enhance the vdW stacking energy to an eV-level for DNA base pairs. There is cohesion even without a backbone.*

Nano-DNA interactions

As a model we consider the self-organization of two-base-pair nanoDNA building blocks and allowing full relaxations in vdW-DF-cx (with an effective model of the backbone charging).



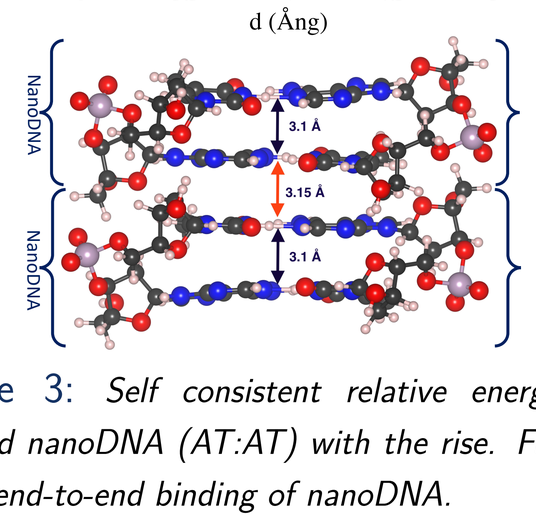


Figure 3: *Self consistent relative energies of stacked nanoDNA (AT:AT) with the rise. Fully relaxed end-to-end binding of nanoDNA.*

References

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NanoDNA stacking: Self-assembly of a genome?

There are observations that even ultra-short nanoDNA segments will spontaneously form a liquid crystal phase (that formally requires an aspect ratio of about 50). This means that nanoDNA self-organizes into long base-pair sequences, through an end-to-end stacking. We find that the flatness of the base pairs produces a large > 0.6 eV end-to-end binding of nanoDNAs (even in the absence of a phosphate linker group). We also find minimal lateral interactions. Our findings that van der Waals forces drive a nanoDNA stacking is consistent with a hypothesis of self-assembling genomes facilitated in liquid-crystal phases.