

Supplementary Information

Helium cluster ions: a coupled-monomers approach to weak covalent networks

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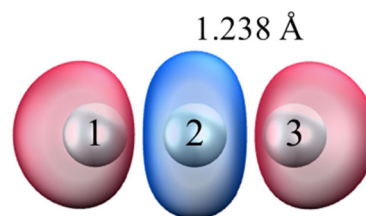
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Remote interactions in selected He_n^+ structures

Linear He_3^+ , Fig. 3(b)

1) From the CCSD optimisation, $r_{1,3} = 2 \times r_{1,2} = 2.286$ d.u.

2) From eqn (7) and the He_2^+ curve in Fig. 4, $h_{1,3} = -V(r_{1,3}) = 0.104$ d.u., while $h_{1,2} = h_{2,3} = -\beta(\chi_{1,2})$ per eqn (5).



3) Treating the remote interaction as a first-order perturbation, assume that the IMO is defined by the nearest-neighbour interactions only:

$$|\phi\rangle = (1/2, -1/\sqrt{2}, 1/2)$$

Then, $\rho_{1,2} = \rho_{2,3} = -1/(2\sqrt{2})$ and $\rho_{1,3} = 1/4$, while the corresponding absolute order for the nearest-neighbour bonds $\chi_{1,2} = \chi_{2,3} = 1/(2\sqrt{2}) \approx 0.354$ [eqn (4)].

4) Per eqn (1),

$$\Delta E_M = -2\rho_{1,2}h_{1,2} - 2\rho_{2,3}h_{2,3} - 2\rho_{1,3}h_{1,3} = -2 \times 2\rho_{1,2}h_{1,2} - 2\rho_{1,3}h_{1,3}$$

[eqn (10) in the main paper], where $h_{1,2} = h_{2,3} = -\beta(0.354)$ and $h_{1,3} = 0.104$ d.u. (see above).

Using the CCSD value of $\Delta E_M = 1.066$ for He_3^+ (Table 1), this yields:

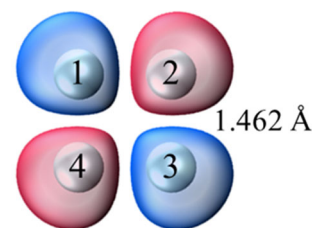
$$\beta(0.354) = -0.791 \text{ d.u.}$$

This corrected value of β for $\chi = 0.354$ is included in Table 1 and indicated by red circle ‘b’ in Fig. 9.

5) The 1-3 interaction in He_3^+ is destabilising and amounts to approximately -10% of each of the 1-2 and 2-3 nearest-neighbour bonds (calculated as $\rho_{1,3}h_{1,3}/\rho_{1,2}h_{1,2}$), i.e., it is 10 times weaker and opposite in character (antibonding). Since there are two bonds and only one remote pair, the overall destabilising effect of the the remote forces in the trimer is $\sim 5\%$ of ΔE_M . This small magnitudes affirms the validity of the perturbative approach to these interactions.

Square He_4^+ , Fig. 3(c)

1) From the CCSD optimisation, $r_{1,2} = r_{2,3} = r_{3,4} = r_{4,1} = 1.462 \text{ \AA} = 1.350 \text{ d.u.}$ and $r_{1,3} = r_{2,4} = \sqrt{2}r_{1,2} = 1.909 \text{ d.u.}$



2) From eqn (7) and the He_2^+ curve in Fig. 4, $h_{1,3} = h_{2,4} = -V(r_{1,3}) = 0.237 \text{ d.u.}$, while $h_{1,2} = h_{2,3} = -\beta(\chi_{1,2})$ per eqn (5).

3) Under the model approximations, the IMO in this case is defined as:

$$|\phi\rangle = (1/2, -1/2, 1/2, -1/2)$$

Then, $\rho_{1,2} = \rho_{2,3} = \rho_{3,4} = \rho_{4,1} = -1/4$ and $\rho_{1,3} = \rho_{2,4} = 1/4$, while the corresponding absolute order for the nearest-neighbour bonds is $\chi = 1/4$ [eqn (4)].

4) Per eqn (1),

$$\Delta E_M = -4 \times 2 \rho_{1,2} h_{1,2} - 2 \times 2 \rho_{1,3} h_{1,3},$$

where $h_{1,2} = -\beta(1/4)$ and $h_{1,3} = 0.237 \text{ d.u.}$ (see above). Using the CCSD value of $\Delta E_M = 0.871 \text{ d.u.}$ for He_4^+ (Table 1), the above yields:

$$\beta(0.250) = -0.554 \text{ d.u.}$$

This corrected β for $\chi = 1/4$ is included in Table 1 and indicated by red circle ‘c’ in Fig. 9.

5) The remote interactions in He_4^+ are destabilising and amount to -21% of the nearest-neighbour bonds, calculated as the ratio of the second and first terms on the right side of the first equation in part (4) above. Stated in another way, remote interactions constitute -25% of total ΔE_M . This is the case where the first-order perturbative approach is least justified of all cases considered here.

Hexagonal He_6^+ , Fig. 4(d)

1) Under the model approximations, the IMO is defined as:

$$|\phi\rangle = (1/\sqrt{6}, -1/\sqrt{6}, 1/\sqrt{6}, -1/\sqrt{6}, 1/\sqrt{6}, -1/\sqrt{6})$$

For the nearest-neighbour ($s = 1$) and third-degree separation ($s = 3$) pairs, the Hückel and absolute bond orders are all given by:

$$\rho_{i,i+1} = \rho_{i,i+3} = -1/6, \quad \chi_{i,i+1} = \chi_{i,i+3} = 1/6$$

reflecting h-bonding interactions. The degree of separation is defined in the main article as $s = |i - j|$. Hereafter, for the model cyclic structures, we assume that the monomer indices are defined on a closed n -loop. For example, in the case of $n = 6$, $6 + 1 = 1$, $5 + 2 = 1$, and $6 + 3 = 3$.

The second-degree ($s = 2$) pairs are all described by the opposite-sign bond orders, reflecting their h-antibonding interactions:

$$\rho_{i,i+2} = 1/6, \quad \chi_{i,i+2} = -1/6$$

2) From the CCSD optimisation (Table 1), all nearest-neighbour ($s = 1$) bonds have lengths of:

$$r_{i,i+1} = 1.620 \text{ \AA} = 1.496 \text{ d.u.}$$

The second-degree ($s = 2$) bondlengths are given by:

$$r_{i,i+2} = \sqrt{3}r_{1,2} = 2.291 \text{ d.u.}$$

The third-degree ($s = 3$) bondlengths are given by:

$$r_{i,i+3} = 2r_{1,2} = 2.992 \text{ d.u.}$$

3) Per eqn (5), the nearest-neighbour bond integrals are given by:

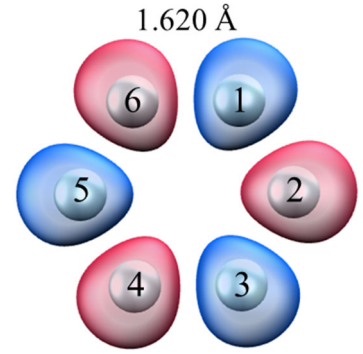
$$h_{i,i+1} = -\beta(\chi_{i,i+1}) = -\beta(1/6)$$

From eqn (7) and the He_2^+ curve in Fig. 4, the second-degree ($s = 2$) and third-degree ($s = 3$) bond integrals are equal to, respectively:

$$h_{i,i+2} = -V(r_{i,i+2}) = -V(2.291 \text{ d.u.}) = 0.0529 \text{ d.u.}$$

$$h_{i,i+3} = -V(r_{i,i+3}) = -V(2.992 \text{ d.u.}) = 0.0214 \text{ d.u.}$$

4) In the hexagonal structure of comprised of 6 identical monomers, there are **six** unique but equivalent nearest-neighbour ($s = 1$) pairs in total (counting the exchange pairs as one), in addition



to **six** second-degree ($s = 2$) pairs and **three** third-degree ($s = 3$) pairs.* Therefore, per eqn (1),

$$\Delta E_M = -6 \times 2 \rho_{i,i+1} h_{i,i+1} - 6 \times 2 \rho_{i,i+2} h_{i,i+2} - 3 \times 2 \rho_{i,i+3} h_{i,i+3}$$

where $h_{i,i+1} = -\beta(1/6)$, while all other bond integrals and the corresponding Hückel bond orders are determined in parts (3) and (1) above. Using $\Delta E_M = 0.666$ d.u. from Table 1, the above yields:

$$\beta(0.167) = -0.375 \text{ d.u.}$$

This corrected β for $\chi = 1/6$ is included in Table 1 and indicated by red circle 'd' in Fig. 9.

5) The remote interactions in He_6^+ are destabilising and amount to -11% of the nearest-neighbour bonds or -13% of total ΔE_M .

Hendecagonal He_{10}^+ , Fig. 4(e)

1) Under the model approximations, the IMO is defined as:

$$|\phi\rangle = (1/\sqrt{10}, -1/\sqrt{10}, \dots, 1/\sqrt{10}, -1/\sqrt{10})$$

For the nearest-neighbour ($s = 1$) and third- ($s = 3$) and fifth- ($s = 5$) degree of separation pairs, the Hückel and absolute bond orders are all given by:

$$\rho_{i,i+1} = \rho_{i,i+3} = \rho_{i,i+5} = -1/10$$

$$\chi_{i,i+1} = \chi_{i,i+3} = \chi_{i,i+5} = 1/10$$

(h-bonding interactions).

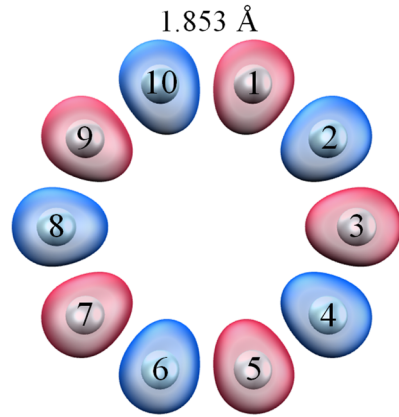
The second- ($s = 2$) and fourth- ($s = 4$) degree of separation pairs are all described by the opposite-sign bond orders (compared to the above), reflecting the h-antibonding interactions:

$$\rho_{i,i+2} = \rho_{i,i+4} = 1/10$$

$$\chi_{i,i+2} = \chi_{i,i+4} = -1/10$$

2) From CCSD optimisation (Table 1), all nearest-neighbour ($s = 1$) bondlengths are:

$$s = 1: \quad r_{i,i+1} = 1.853 \text{ \AA} = 1.712 \text{ d.u.}$$



* The binomial coefficient check: the total number of pairs in a six-membered structure is $C(6,2) = \frac{6!}{2!(6-2)!} = 15$. The above pair counts do indeed add up to this number: $6 + 6 + 3 = 15$.

The bondlengths of higher degrees of separations are:

$$\begin{aligned}
 s = 2: & \quad r_{i,i+2} = 3.256 \text{ d.u.} \\
 s = 3: & \quad r_{i,i+3} = 4.482 \text{ d.u.} \\
 s = 4: & \quad r_{i,i+4} = 5.269 \text{ d.u.} \\
 s = 5: & \quad r_{i,i+5} = 5.540 \text{ d.u.}
 \end{aligned}$$

3) Per eqn (5), the nearest-neighbour bond integrals are given by:

$$s = 1: \quad h_{i,i+1} = -\beta(\chi_{i,i+1}) = -\beta(1/10)$$

From eqn (7) and the He_2^+ curve in Fig. 3, the higher-degree ($s > 1$) bond integrals are equal to:

$$\begin{aligned}
 s = 2: & \quad h_{i,i+2} = -V(r_{i,i+2}) = -V(3.256 \text{ d.u.}) = 0.0207 \text{ d.u.} \\
 s = 3: & \quad h_{i,i+3} = -V(r_{i,i+3}) = -V(4.482 \text{ d.u.}) = 0.000727 \text{ d.u.} \\
 s = 4: & \quad h_{i,i+4} = -V(r_{i,i+4}) = -V(5.269 \text{ d.u.}) = 0.000121 \text{ d.u.} \\
 s = 5: & \quad h_{i,i+5} = -V(r_{i,i+5}) = -V(5.540 \text{ d.u.}) = 0.000065 \text{ d.u.}
 \end{aligned}$$

4) In the hendecagonal structure of 10 identical monomers, there are **10** unique but equivalent nearest-neighbour ($s = 1$) pairs, **10** second-degree ($s = 2$) pairs, **10** third-degree ($s = 3$) pairs, **10** fourth-degree ($s = 4$) pairs, and **5** fifth-degree ($s = 5$) pairs.[†] Therefore, per eqn (1),

$$\begin{aligned}
 \Delta E_M = & -\mathbf{10} \times 2 \rho_{i,i+1} h_{i,i+1} - \mathbf{10} \times 2 \rho_{i,i+2} h_{i,i+2} - \mathbf{10} \times 2 \rho_{i,i+3} h_{i,i+3} \\
 & - \mathbf{10} \times 2 \rho_{i,i+4} h_{i,i+4} - \mathbf{5} \times 2 \rho_{i,i+5} h_{i,i+5}
 \end{aligned}$$

where $h_{i,i+1} = -\beta(1/10)$, while all other bond integrals and the corresponding Hückel bond orders are given in parts (3) and (1) above. Using $\Delta E_M = 0.408 \text{ d.u.}$ from Table 1, the above yields:

$$\beta(0.100) = -0.229 \text{ d.u.}$$

This corrected β for $\chi = 1/10$ is included in Table 1 and indicated by red circle 'e' in Fig. 9.

5) The remote interactions in He_{10}^+ are destabilising and amount to -11% of the nearest-neighbour bonds or -12% of total ΔE_M .

[†] The binomial coefficient check: $10 + 10 + 10 + 10 + 5 = 45 = C(10,2) = \frac{10!}{2!(10-2)!}$.