

Electronic supplementary material

Comparison of DAFH and FALDI-like approaches

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Section S1. Geometry for B₂H₆

Table S1 Cartesian coordinates (in Å) used for symmetry-unique atoms in B₂H₆ (*D*_{2h}), with the inversion center taken as the origin. H_b is a bridging H atom and H_t is a terminal one.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
B	0.888375	0	0
H _b	0	0	0.973751
H _t	1.463157	1.035737	0

Section S2. Additional results for H₂

Figure S1. Dominant DAFH functions associated with the domain of one of the H atoms in H₂ at three representative nuclear separations, generated using the one-electron approximation. Also shown for each function is the corresponding occupation number as well as the proportion of $k_{\text{HH}'} = \frac{1}{2} \text{SEDI}(\text{H}, \text{H}')$ which can be assigned to a term P_i (see equation 6) that involves this function.

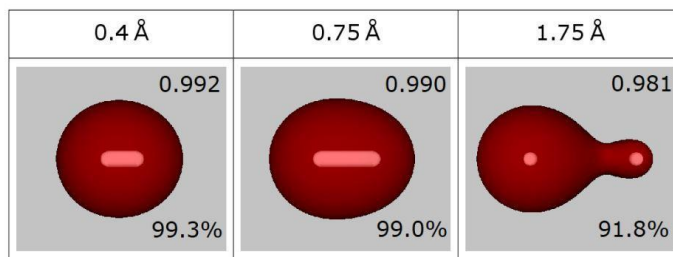
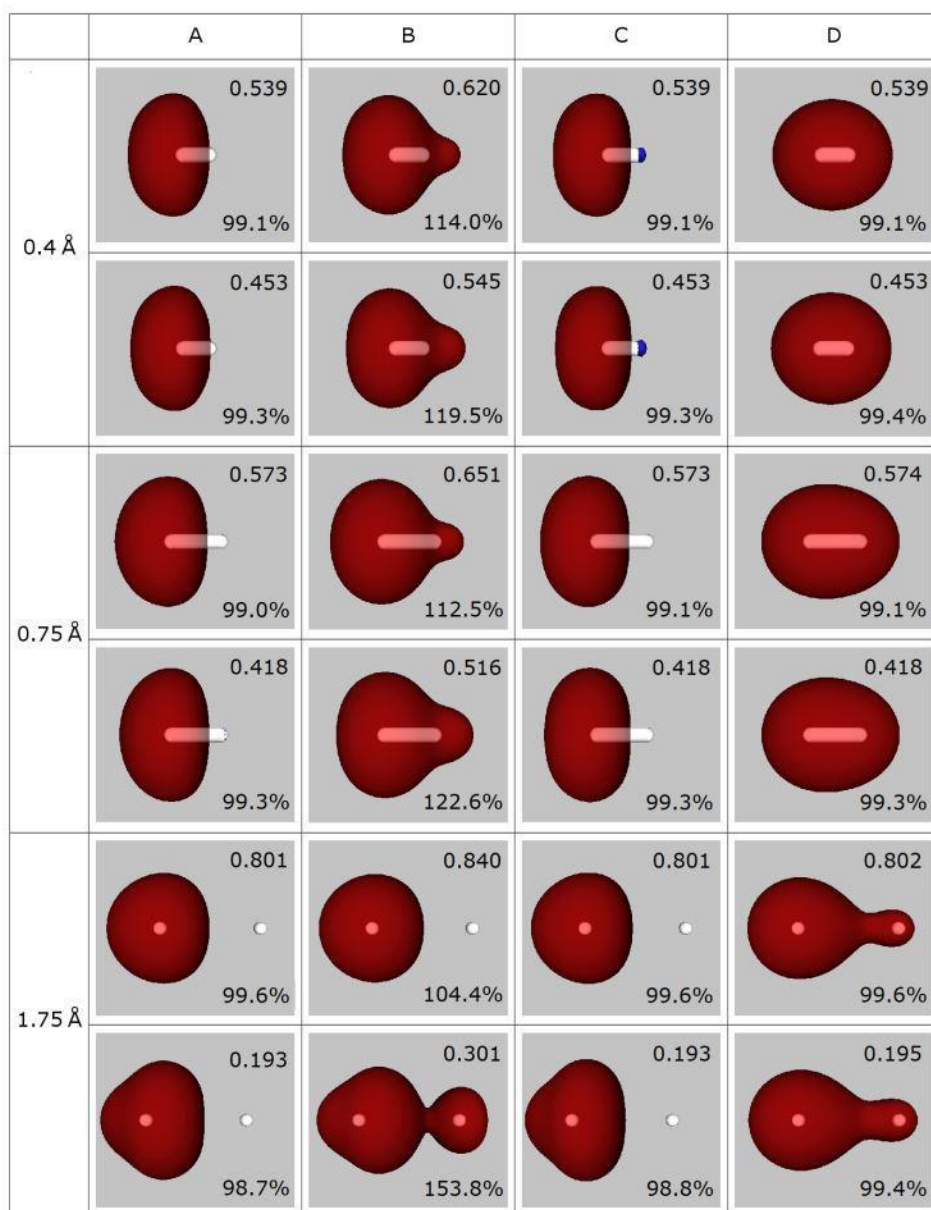


Figure S2. Dominant FALDI-like functions associated with the domain of one of the H atoms in H₂ at three representative nuclear separations, together with their eigenvalues and relative contributions to the relevant k values, calculated using the one-electron approximation. For each of these values of R , the first row corresponds to partitioning of k_{HH} and the second one to partitioning of $k_{\text{HH}'}$. Columns are labelled A-D according to the variant of the approach, as described in the text.



Section S3. Additional results for N₂

Figure S3. Dominant DAFH functions associated with the domain of one of the N atoms in N₂ at three representative nuclear separations, generated using the one-electron approximation. Also shown for each function is the corresponding occupation number as well as the proportion of $k_{NN'} = \frac{1}{2} \text{SEDI}(N, N')$ which can be assigned to a term P_i (see equation 6) that involves this function.

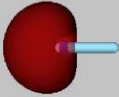
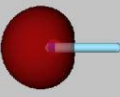
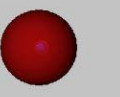
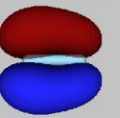
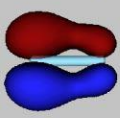
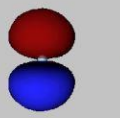
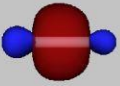
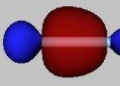
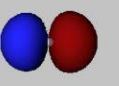
1.1 Å	1.5 Å	2.5 Å
 1.982 51.3%	 1.979 47.5%	 1.993 40.4%
 0.997 2× 16.8%	 0.992 2× 18.4%	 0.997 2× 20.1%
 0.999 14.9%	 0.997 15.7%	 0.987 19.3%

Figure S4. Dominant Scheme B FALDI-like functions that can be associated (by visual inspection) with the domain of one of the N atoms in N₂ at three representative nuclear separations, together with their eigenvalues and relative contributions to the relevant *k* values, generated using the full calculation.

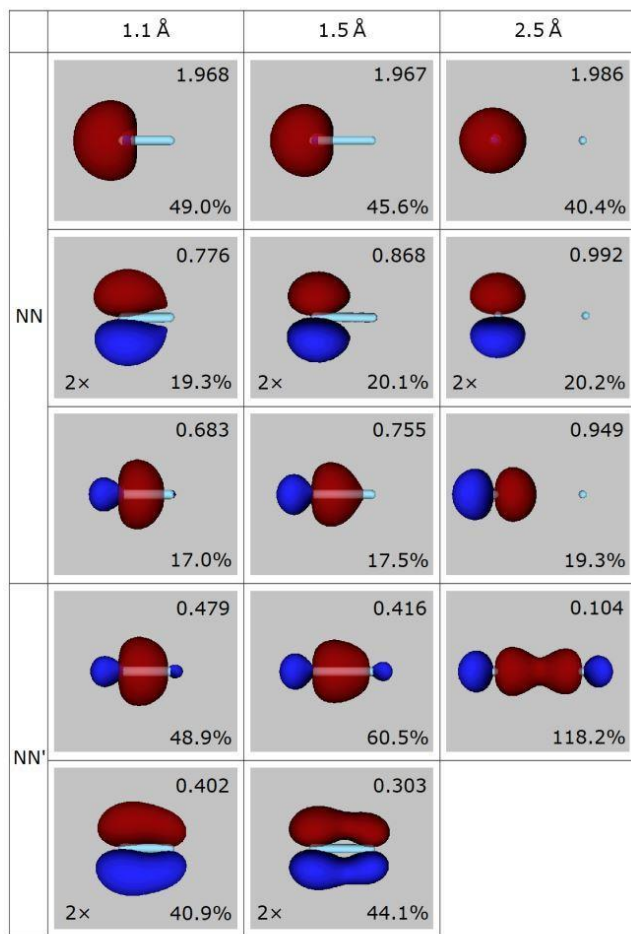


Figure S5. Dominant Scheme C FALDI-like functions that can be associated (by visual inspection) with the domain of one of the N atoms in N_2 at three representative nuclear separations, together with their eigenvalues and relative contributions to the relevant k values, generated using the full calculation.

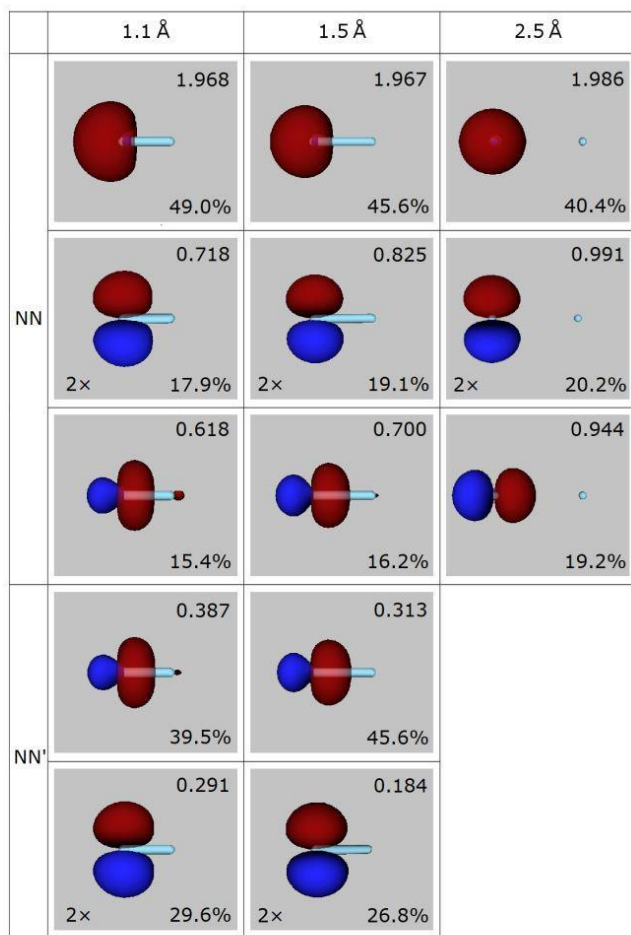


Figure S6. Dominant Scheme D FALDI-like functions that can be associated (by visual inspection) with the domain of one of the N atoms in N_2 at three representative nuclear separations, together with their eigenvalues and relative contributions to the relevant k values, generated using the full calculation.

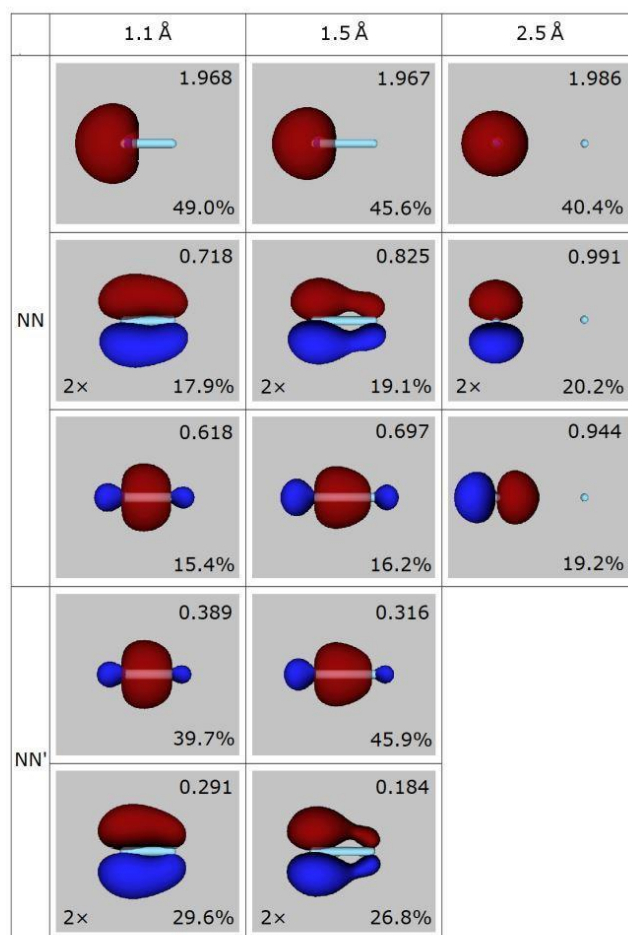


Figure S7. Dominant Scheme A FALDI-like functions that can be associated (by visual inspection) with the domain of one of the N atoms in N_2 at three representative nuclear separations, together with their eigenvalues and relative contributions to the relevant k values, calculated using the one-electron approximation.

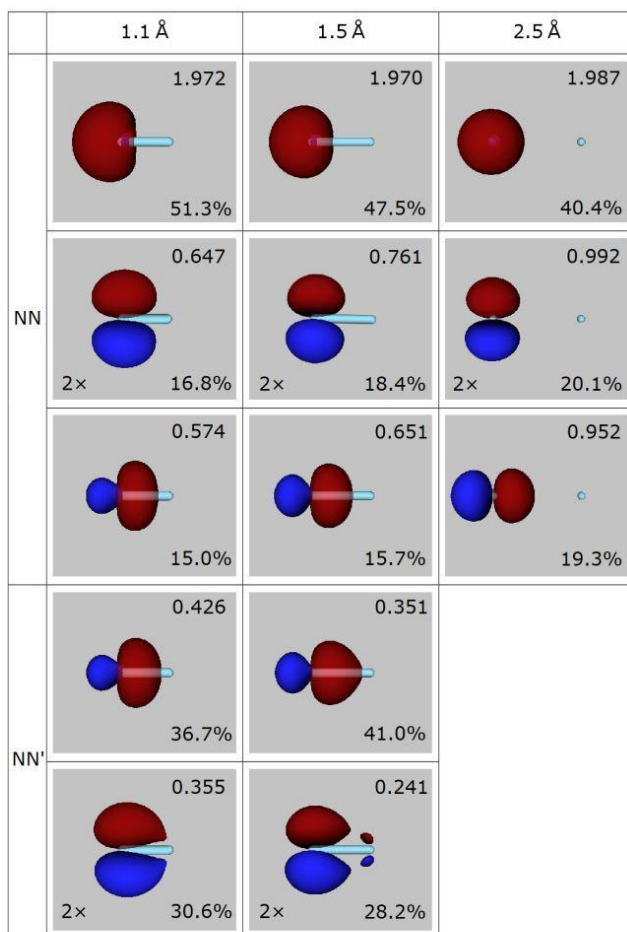


Figure S8. Dominant Scheme B FALDI-like functions that can be associated (by visual inspection) with the domain of one of the N atoms in N_2 at three representative nuclear separations, together with their eigenvalues and relative contributions to the relevant k values, calculated using the one-electron approximation.

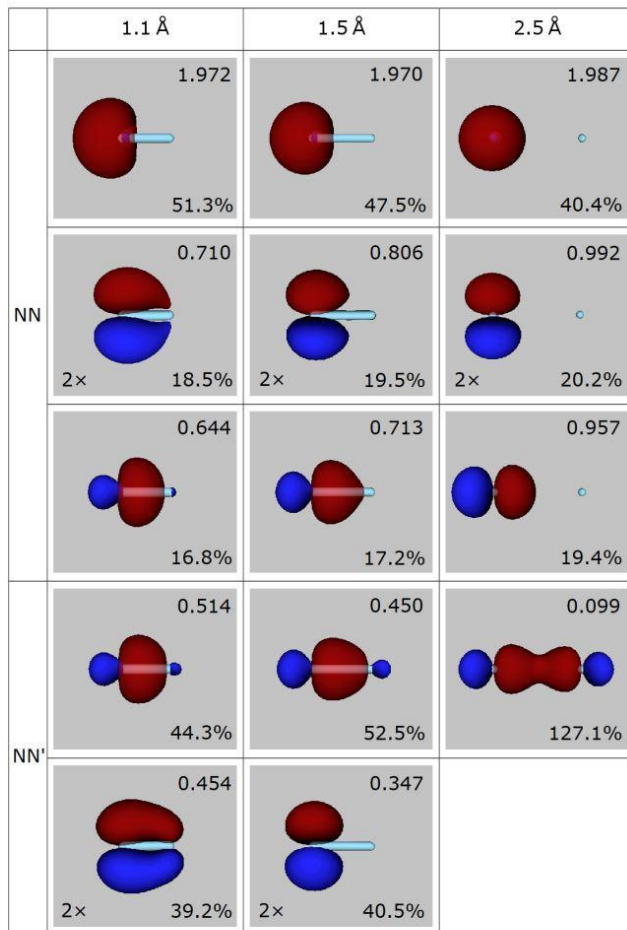


Figure S9. Dominant Scheme C FALDI-like functions that can be associated (by visual inspection) with the domain of one of the N atoms in N_2 at three representative nuclear separations, together with their eigenvalues and relative contributions to the relevant k values, calculated using the one-electron approximation.

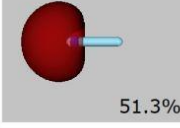
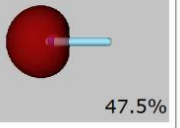
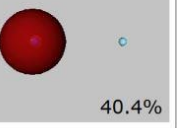
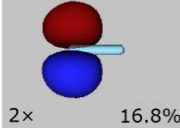
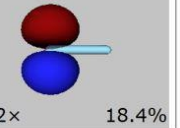
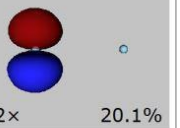
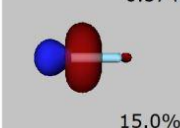
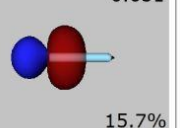
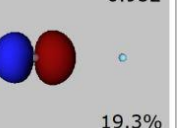
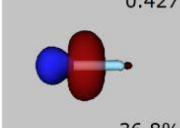
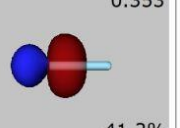
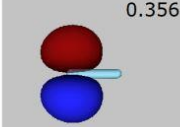
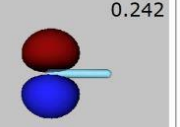
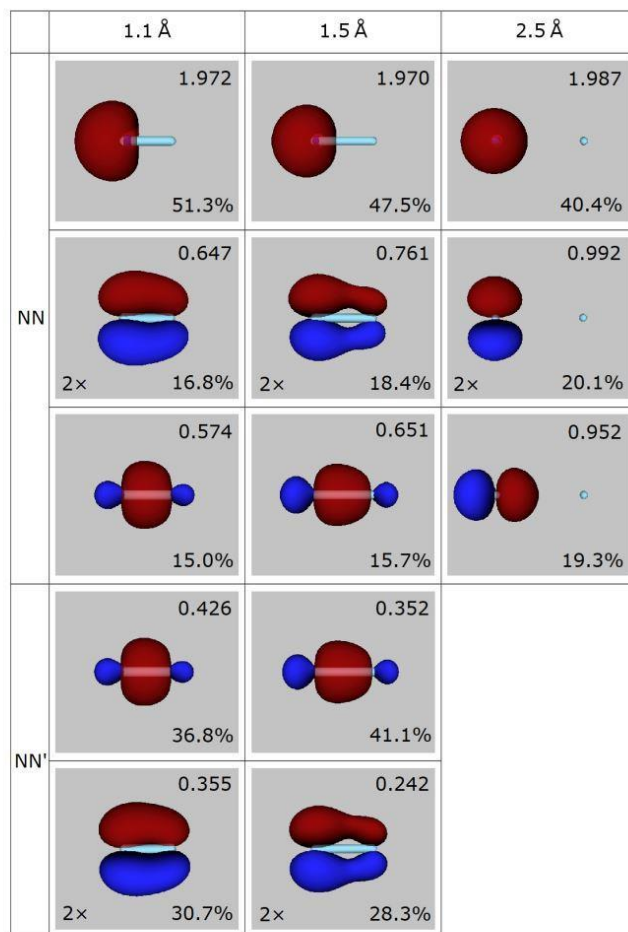
	1.1 Å	1.5 Å	2.5 Å
NN	 1.972 51.3%	 1.970 47.5%	 1.987 40.4%
	 0.647 2× 16.8%	 0.761 2× 18.4%	 0.992 2× 20.1%
	 0.574 15.0%	 0.651 15.7%	 0.952 19.3%
NN'	 0.427 36.8%	 0.353 41.2%	
	 0.356 2× 30.7%	 0.242 2× 28.3%	

Figure S10. Dominant Scheme D FALDI-like functions that can be associated (by visual inspection) with the domain of one of the N atoms in N_2 at three representative nuclear separations, together with their eigenvalues and relative contributions to the relevant k values, calculated using the one-electron approximation.



Section S4. Additional results for B₂H₆

Figure S11. Dominant DAFH functions (first column) and Scheme B FALDI-like functions (second and third columns) for B₂H₆, together with their eigenvalues and relative contributions to relevant k values, generated using the full calculation. The specific domains used for each of these functions are the same as those in Figure 5 and are identified in the main text, expect that the additional function depicted in the third column is associated with one of the B domains.

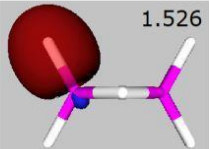
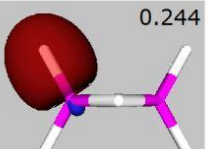
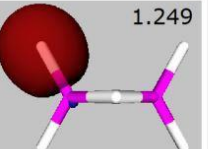
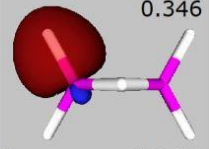
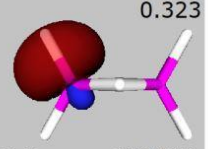
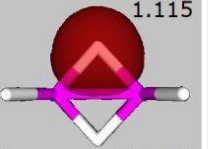
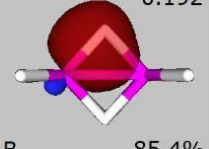
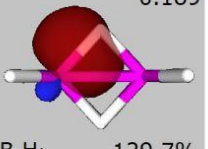
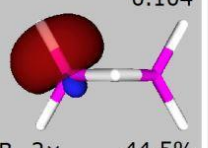
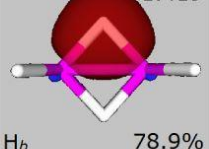
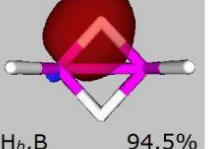
DAFH	$\Omega\Omega'$	$\Omega\Omega$
 <p>1.526 H_t 93.8%</p>	 <p>0.244 H_t,B 100.8%</p>	 <p>1.249 H_t 102.2%</p>
 <p>0.346 B 95.4%</p>	 <p>0.323 B, H_t 133.3%</p>	 <p>1.115 H_b 101.8%</p>
 <p>0.192 B 85.4%</p>	 <p>0.189 B, H_b 129.7%</p>	 <p>0.104 B 2× 44.5%</p>
 <p>1.419 H_b 78.9%</p>	 <p>0.138 H_b,B 94.5%</p>	

Figure S12. Dominant DAFH functions (first column) and Scheme C FALDI-like functions (second and third columns) for B_2H_6 , together with their eigenvalues and relative contributions to relevant k values, generated using the full calculation. The specific domains used for each of these functions are the same as those in Figure 5 and are identified in the main text.

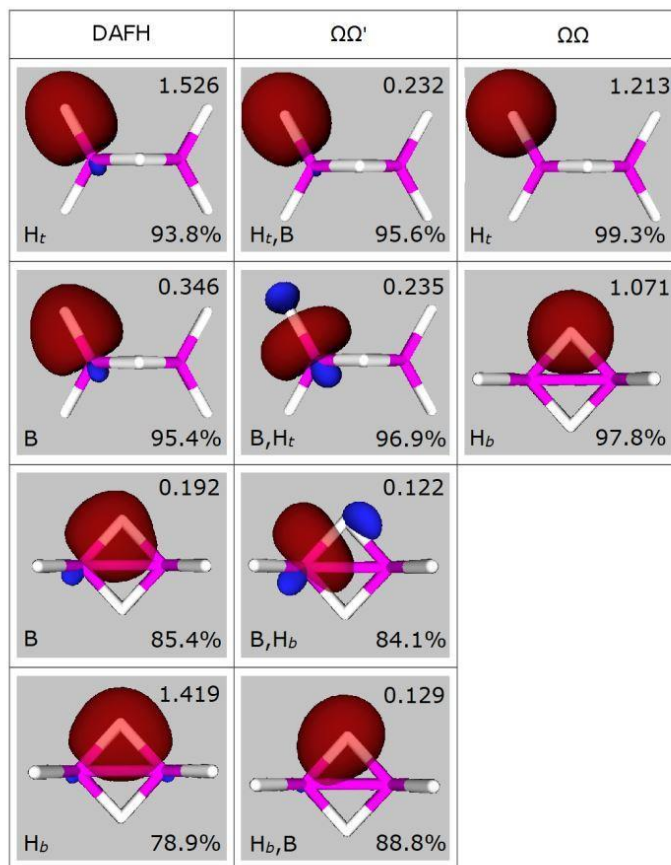


Figure S13. Dominant DAFH functions (first column) and Scheme D FALDI-like functions (second and third columns) for B_2H_6 , together with their eigenvalues and relative contributions to relevant k values, generated using the full calculation. The specific domains used for each of these functions are the same as those in Figure 5 and are identified in the main text.

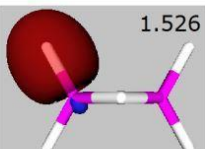
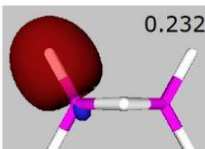
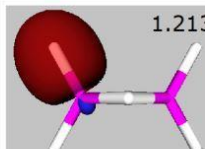
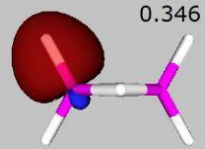
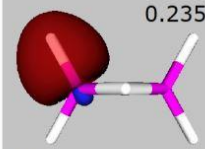
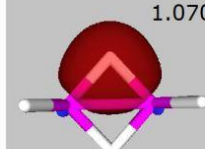
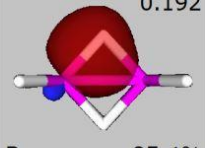
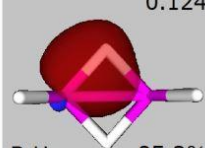
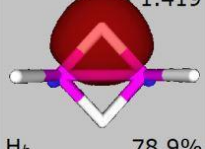
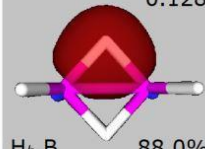
DAFH	$\Omega\Omega'$	$\Omega\Omega$
 <p>1.526 H_t 93.8%</p>	 <p>0.232 H_t, B 95.6%</p>	 <p>1.213 H_t 99.2%</p>
 <p>0.346 B 95.4%</p>	 <p>0.235 B, H_t 97.0%</p>	 <p>1.070 H_b 97.7%</p>
 <p>0.192 B 85.4%</p>	 <p>0.124 B, H_b 85.3%</p>	
 <p>1.419 H_b 78.9%</p>	 <p>0.128 H_b, B 88.0%</p>	

Figure S14. Dominant DAFH functions (first column) and Scheme A FALDI-like functions (second and third columns) for B_2H_6 , together with their eigenvalues and relative contributions to relevant k values, calculated using the one-electron approximation. The specific domains used for each of these functions are the same as those in Figure 5 and are identified in the main text.

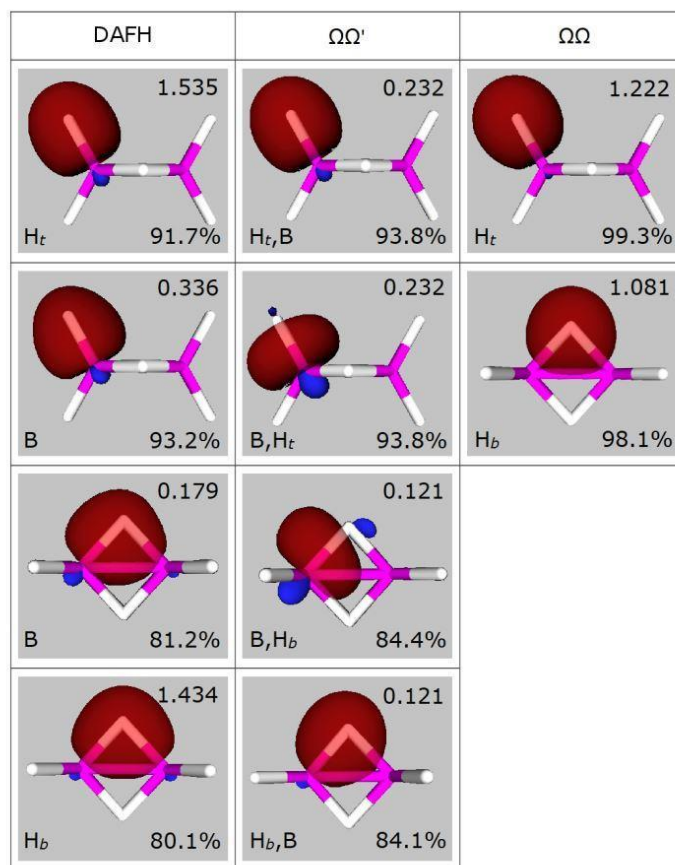


Figure S15. Dominant DAFH functions (first column) and Scheme B FALDI-like functions (second and third columns) for B_2H_6 , together with their eigenvalues and relative contributions to relevant k values, calculated using the one-electron approximation. The specific domains used for each of these functions are the same as those in Figure 5 and are identified in the main text.

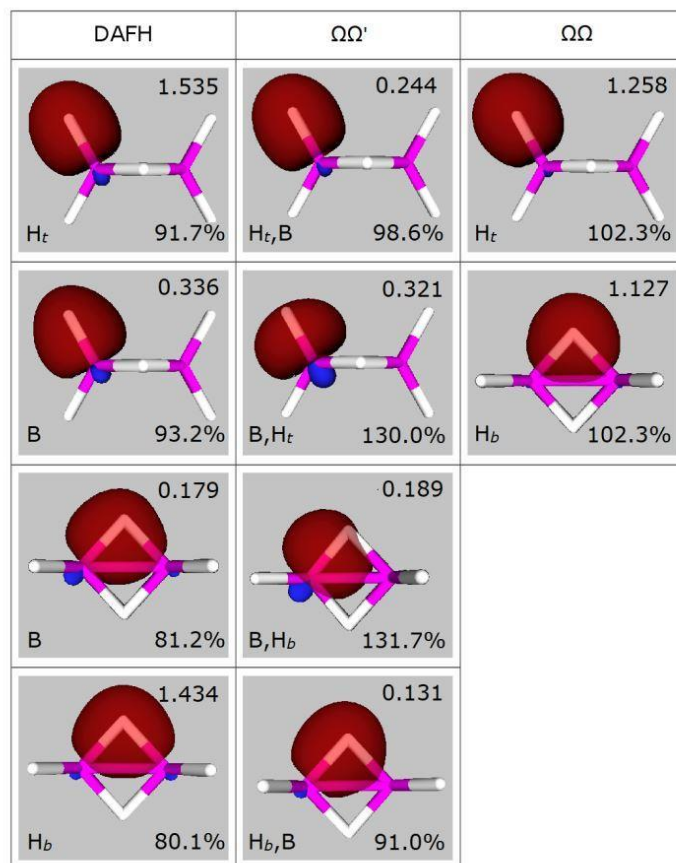


Figure S16. Dominant DAFH functions (first column) and Scheme C FALDI-like functions (second and third columns) for B_2H_6 , together with their eigenvalues and relative contributions to relevant k values, calculated using the one-electron approximation. The specific domains used for each of these functions are the same as those in Figure 5 and are identified in the main text.

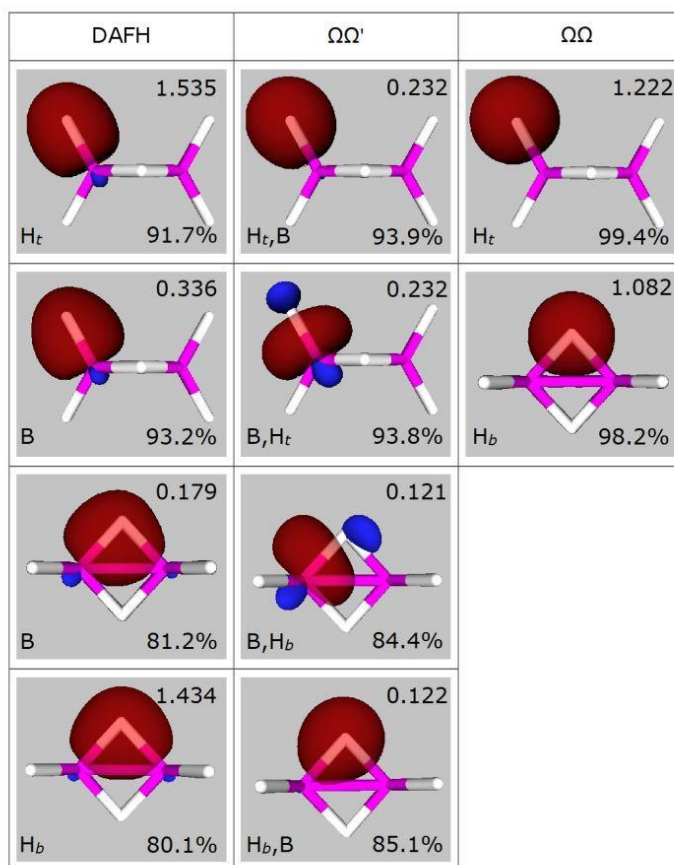


Figure S17. Dominant DAFH functions (first column) and Scheme D FALDI-like functions (second and third columns) for B_2H_6 , together with their eigenvalues and relative contributions to relevant k values, calculated using the one-electron approximation. The specific domains used for each of these functions are the same as those in Figure 5 and are identified in the main text.

