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A One-Electron Approximation to Domain-Averaged Fermi Hole Analysis

(Electronic Supplementary Information)

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Table S1

R-dependence of non-trivial eigenvalues resulting from pDAFH analysis for H_2. The corresponding DAFH eigenvalues practically coincide (differences in the fifth decimal place).

R / Å	ε_1^{σ}	ε_2^{σ}	ε_3^{σ}	ε_1^{π}, ε_2^{π}
0.75	0.990	0.003	0.002	0.002
1.00	0.988	0.005	0.003	0.002
1.25	0.986	0.008	0.002	0.002
1.50	0.983	0.013	0.002	0.001
2.00	0.982	0.017		
2.50	0.988	0.011		
3.00	0.994	0.006		

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Table S2

Overlap integrals between pDAFH and DAFH functions for H_2. For a given value of *R*, the rows correspond to the different pDAFH functions, always for domain H1, in strict order of decreasing eigenvalue. The columns correspond to the different DAFH functions, again in strict order of decreasing eigenvalue, with the left-hand block being for domain H1 and the right-hand block for domain H2.

R=0.75 Å

1.000	0.059	0.112	0.000	0.000		0.984	0.140	-0.262	0.000	0.000
-0.032	0.708	-0.649	0.000	0.000		-0.075	0.961	0.275	0.000	0.000
0.127	0.575	0.714	0.000	0.000		0.296	-0.264	0.866	0.000	0.000
0.000	0.000	0.000	0.949	0.000		0.000	0.000	0.000	1.000	0.000
0.000	0.000	0.000	0.000	0.949		0.000	0.000	0.000	0.000	1.000

R=1.00 Å

1.000	-0.182	-0.036	0.000	0.000		0.964	0.426	-0.083	0.000	0.000
-0.189	0.893	0.287	0.000	0.000		-0.437	0.802	-0.031	0.000	0.000
0.002	-0.217	0.922	0.000	0.000		0.006	0.199	0.985	0.000	0.000
0.000	0.000	0.000	0.937	0.000		0.000	0.000	0.000	1.000	0.000
0.000	0.000	0.000	0.000	0.937		0.000	0.000	0.000	0.000	1.000

R=1.25 Å

1.000	-0.247	-0.032	0.000	0.000		0.925	0.591	-0.072	0.000	0.000
-0.254	0.938	0.208	0.000	0.000		-0.597	0.629	0.032	0.000	0.000
0.002	-0.141	0.923	0.000	0.000		0.010	0.113	0.995	0.000	0.000
0.000	0.000	0.000	0.921	0.000		0.000	0.000	0.000	1.000	0.000
0.000	0.000	0.000	0.000	0.921		0.000	0.000	0.000	0.000	1.000

R=1.50 Å

1.000	-0.293	-0.035	0.000	0.000		0.852	0.744	-0.076	0.000	0.000
-0.302	0.958	0.183	0.000	0.000		-0.751	0.411	0.060	0.000	0.000
-0.003	-0.111	0.922	0.000	0.000		0.004	0.093	0.996	0.000	0.000
0.000	0.000	0.000	0.901	0.000		0.000	0.000	0.000	1.000	0.000
0.000	0.000	0.000	0.000	0.901		0.000	0.000	0.000	0.000	1.000

R=2.00 Å

1.000	-0.262	0.594	0.928
-0.272	0.980	-0.932	0.101

R=2.50 Å

1.000	-0.153	0.321	0.983
-0.158	0.993	-0.984	0.018

R=3.00 Å

1.000	-0.076	0.155	0.996
-0.078	0.998	-0.996	0.003

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Table S3

R-dependence of non-trivial eigenvalues resulting from pDAFH and DAFH analysis for the N_2. For each bond length, *R*, the upper row corresponds to pDAFH and the lower one to DAFH analysis.

R / a_0	ε_1^{σ}	ε_2^{σ}	ε_3^{σ}	ε_4^{σ}	$\varepsilon_1^{\pi}, \varepsilon_2^{\pi}$	$\varepsilon_3^{\pi}, \varepsilon_4^{\pi}$
1.75	1.980	0.999	0.015	0.001	0.998	0.004
	1.977	1.006	0.028		1.019	
2.00	1.982	0.999	0.012	0.002	0.997	0.006
	1.978	1.008	0.023		1.025	
2.50	1.981	0.998	0.013	0.001	0.995	0.009
	1.977	1.014	0.036		1.035	
3.00	1.979	0.996	0.017		0.991	0.012
	1.975	1.013	0.039		1.030	
3.50	1.983	0.990	0.024		0.990	0.012
	1.979	0.992	0.042		1.003	
4.00	1.986	0.985	0.028		0.993	0.008
	1.984	0.970	0.045		0.993	0.008
4.50	1.991	0.986	0.023		0.996	0.004
	1.990	0.975	0.033	0.002	0.995	0.005
5.00	1.994	0.989	0.016		0.998	0.002
	1.994	0.984	0.021	0.002	0.997	0.003

Table S4

Overlap integrals between pDAFH and DAFH functions for N_2. For a given value of *R*, the rows correspond to the different pDAFH functions for domain N1 and the columns to the different DAFH functions for the same domain, always in strict order of decreasing eigenvalue.

R=1.75 a_0

1.000	0.000	0.000	-0.008	-0.006
0.003	0.000	0.000	0.999	-0.101
0.000	0.998	0.000	0.000	0.000
0.000	0.000	0.998	0.000	0.000
-0.001	0.000	0.000	0.002	-0.914
0.000	0.000	-0.121	0.000	0.000
0.000	-0.121	0.000	0.000	0.000
0.000	0.000	0.000	-0.043	0.442

R=2.00 a_0

1.000	0.000	0.000	-0.011	0.008
0.004	0.000	0.000	0.999	0.131
0.000	0.998	0.000	0.000	0.000
0.000	0.000	0.998	0.000	0.000
0.000	0.000	0.000	0.012	0.942
0.000	-0.154	0.000	0.000	0.000
0.000	0.000	-0.154	0.000	0.000
-0.002	0.000	0.000	-0.065	-0.410

R=2.50 a_0

1.000	0.000	0.000	0.017	-0.011
-0.004	0.000	0.000	0.998	0.181
0.000	0.998	0.000	0.000	0.000
0.000	0.000	0.998	0.000	0.000
-0.001	0.000	0.000	0.065	0.996
0.000	-0.225	0.000	0.000	0.000
0.000	0.000	-0.225	0.000	0.000
0.003	0.000	0.000	-0.120	-0.159

R=3.00 a_0

1.000	0.000	0.000	0.020	-0.009
-0.002	0.000	0.000	0.999	0.206
0.000	0.999	0.000	0.000	0.000
0.000	0.000	0.999	0.000	0.000
0.001	0.000	0.000	-0.143	-0.994
0.000	-0.278	0.000	0.000	0.000
0.000	0.000	-0.278	0.000	0.000

Table S4 (continued)

R=3.50 a_0

1.000	0.000	0.000	0.018	0.006
0.000	1.000	0.000	0.000	0.000
0.000	0.000	1.000	0.000	0.000
0.005	0.000	0.000	1.000	-0.238
-0.001	0.000	0.000	-0.233	0.995
0.000	-0.231	0.000	0.000	0.000
0.000	0.000	-0.231	0.000	0.000

R=4.00 a_0

1.000	0.000	0.000	0.014	-0.001	0.000	0.000
0.000	1.000	0.000	0.000	0.000	-0.112	0.000
0.000	0.000	1.000	0.000	0.000	0.000	-0.112
0.011	0.000	0.000	1.000	-0.231	0.000	0.000
-0.007	0.000	0.000	-0.214	0.998	0.000	0.000
0.000	-0.112	0.000	0.000	0.000	1.000	0.000
0.000	0.000	-0.112	0.000	0.000	0.000	1.000

R=4.50 a_0

1.000	0.000	0.000	0.009	-0.004	0.000	0.000	0.002
0.000	1.000	0.000	0.000	0.000	-0.053	0.000	0.000
0.000	0.000	1.000	0.000	0.000	0.000	-0.053	0.000
0.010	0.000	0.000	1.000	-0.159	0.000	0.000	0.069
-0.008	0.000	0.000	-0.144	0.993	0.000	0.000	0.114
0.000	-0.053	0.000	0.000	0.000	1.000	0.000	0.000
0.000	0.000	-0.053	0.000	0.000	0.000	1.000	0.000

R=5.00 a_0

1.000	0.000	0.000	0.005	-0.003	0.000	0.000	0.002
0.000	1.000	0.000	0.000	0.000	-0.028	0.000	0.000
0.000	0.000	1.000	0.000	0.000	0.000	-0.028	0.000
0.007	0.000	0.000	1.000	-0.104	0.000	0.000	0.041
-0.006	0.000	0.000	-0.094	0.993	0.000	0.000	0.117
0.000	-0.028	0.000	0.000	0.000	1.000	0.000	0.000
0.000	0.000	-0.028	0.000	0.000	0.000	1.000	0.000

Table S5

R-dependence of non-trivial pDAFH and DAFH eigenvalues for LiH. For each bond length, *R*, the top row corresponds to pDAFH and the second one to DAFH analysis.

R / a_0	Li		H			
	ε_1^{σ}	ε_2^{σ}	ε_1^{σ}	ε_2^{σ}	ε_3^{σ}	ε_1^{π} , ε_2^{π}
2.5	0.107	0.001	1.839	0.025	0.006	0.010
	0.108	0.001	1.838	0.025	0.007	0.010
3.0	0.102		1.841	0.028	0.007	0.010
	0.105		1.839	0.030	0.008	0.009
3.5	0.102		1.835	0.036	0.008	0.009
	0.107		1.829	0.042	0.009	0.008
4.0	0.110		1.816	0.048	0.008	0.008
	0.119		1.806	0.060	0.008	0.007
4.5	0.130		1.782	0.067	0.008	0.006
	0.145		1.764	0.086	0.007	0.006
5.0	0.172		1.721	0.090	0.007	0.005
	0.195	0.001	1.690	0.123	0.006	0.004
5.5	0.250		1.622	0.115	0.006	0.004
	0.288	0.001	1.566	0.173	0.005	0.003
6.0	0.396		1.464	0.130	0.004	0.002
	0.457	0.002	1.368	0.228	0.003	0.002
6.5	0.676	0.002	1.241	0.076	0.003	0.001
	0.757	0.002	1.121	0.197	0.002	
7.0	0.799	0.003	1.139	0.055	0.002	
	0.871	0.001	1.045	0.151		
7.5	0.879	0.003	1.077	0.039		
	0.931		1.015	0.102		
8.0	0.924	0.003	1.040	0.032		
	0.958		1.003	0.070		
9.0	0.971	0.002	1.014	0.012		
	0.983		1.002	0.024		
10.0	0.986	0.001	1.006	0.006		
	0.990		1.002	0.010		

Table S6

Overlap integrals between pDAFH and DAFH functions for LiH. For a given value of *R*, the rows correspond to the different pDAFH functions and the columns to the different DAFH functions, always in strict order of decreasing eigenvalue. The left-hand block is for functions associated with the Li domain and the right-hand block is for the H domain.

R=2.5 a_0

1.000	-0.002
0.016	0.983

1.000	0.037	0.000	0.000	0.086
0.033	0.999	0.000	0.000	-0.001
0.000	0.000	1.000	0.000	0.000
0.000	0.000	0.000	1.000	0.000
0.087	0.086	0.000	0.000	0.999

R=3.0 a_0

1.000

1.000	0.060	0.000	0.000	0.064
0.055	0.997	0.000	0.000	-0.017
0.000	0.000	1.000	0.000	0.000
0.000	0.000	0.000	1.000	0.000
0.068	0.128	0.000	0.000	0.997

R=3.5 a_0

1.000

1.000	0.070	-0.042	0.000	0.000
0.067	0.998	0.013	0.000	0.000
0.000	0.000	0.000	1.000	0.000
0.000	0.000	0.000	0.000	1.000
-0.045	-0.101	0.998	0.000	0.000

R=4.0 a_0

0.999

1.000	0.089	-0.021	0.000	0.000
0.086	1.000	0.002	0.000	0.000
-0.022	-0.041	1.000	0.000	0.000
0.000	0.000	0.000	1.000	0.000
0.000	0.000	0.000	0.000	1.000

R=4.5 a_0

0.997

1.000	0.102	-0.003	0.000	0.000
0.098	1.000	0.000	0.000	0.000
-0.003	0.007	1.000	0.000	0.000
0.000	0.000	0.000	1.000	0.000
0.000	0.000	0.000	0.000	1.000

R=5.0 a_0

0.994	-0.016

1.000	0.132	-0.019	0.000	0.000
0.122	1.000	-0.007	0.000	0.000
-0.021	-0.057	1.000	0.000	0.000
0.000	0.000	0.000	1.000	0.000
0.000	0.000	0.000	0.000	1.000

Table S6 (continued)

R=5.5 a_0

0.991	-0.034

1.000	0.178	-0.039	0.000	0.000
0.151	0.999	-0.003	0.000	0.000
-0.044	-0.082	0.999	0.000	0.000
0.000	0.000	0.000	1.000	0.000
0.000	0.000	0.000	0.000	1.000

R=6.0 a_0

0.987	-0.033

0.999	0.258	-0.036	0.000	0.000
0.178	0.998	0.074	0.000	0.000
-0.047	-0.023	0.999	0.000	0.000
0.000	0.000	0.000	1.000	0.000
0.000	0.000	0.000	0.000	1.000

R=6.5 a_0

0.989	0.015
0.328	0.483

0.995	0.326	0.014	0.000	0.000
0.170	0.998	0.092	0.000	0.000
0.001	0.041	1.000	0.000	0.000
0.000	0.000	0.000	1.000	0.000
0.000	0.000	0.000	0.000	1.000

R=7.0 a_0

0.990	0.020
0.359	0.341

0.992	0.281	-0.022
0.126	0.999	-0.084
0.010	0.031	-1.000

R=7.5 a_0

0.992
0.321

0.993	0.221
0.087	0.999

R=8.0 a_0

0.994
0.262

0.995	0.169
0.060	0.999

R=9.0 a_0

0.998
0.158

0.998	-0.094
-0.030	0.999

R=10.0 a_0

0.999
0.091

0.999	0.053
0.016	0.999

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Table S7

Non-trivial pDAFH and DAFH eigenvalues for selected domains in CH_2Li_2. The upper row corresponds to pDAFH and the lower one to DAFH analysis.

Domain	ε_1	ε_2	ε_3	ε_4	ε_5	ε_6	ε_7	ε_8	ε_9	ε_{10}	ε_{11}	ε_{12}	ε_{13}
C	1.813	1.694	0.947	0.947	0.046	0.032	0.007	0.007	0.007	0.006	0.005	0.005	
	1.810	1.694	0.950	0.950	0.044	0.029	0.009	0.009	0.008	0.006	0.004	0.004	0.001
H	0.983	0.080	0.039	0.012	0.002								
	0.975	0.094	0.049	0.040	0.006	0.003	0.002	0.002					
2×Li	0.111	0.092	0.038	0.007									
	0.113	0.096	0.028	0.028									
1×Li	0.064	0.046	0.014										
	0.064	0.048	0.018	0.006	0.001								

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Table S8

Overlap integrals between pDAFH and DAFH functions for CH_2Li_2. For each of the selected domains, the rows correspond to the different pDAFH functions and the columns to the different DAFH functions for the same domain, always in strict order of decreasing eigenvalue.

C

1.000	0.000	-0.009	0.009	0.000	-0.097	0.048	-0.049	0.000	-0.042	-0.028	0.028	0.000
0.000	0.999	0.000	0.000	0.128	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
-0.002	0.000	1.000	-0.060	0.000	-0.020	-0.002	0.039	0.000	-0.022	0.000	0.117	-0.045
0.002	0.000	-0.060	1.000	0.000	0.020	0.039	-0.002	0.000	0.021	0.117	-0.001	-0.045
0.000	0.059	0.000	0.000	0.999	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
-0.042	0.000	-0.010	0.010	0.000	0.996	-0.008	0.007	0.000	-0.031	0.050	-0.050	0.000
0.000	0.000	0.000	0.000	0.000	0.000	-0.001	-0.001	1.000	0.000	0.000	0.000	0.000
0.015	0.000	-0.014	0.019	0.000	-0.043	-0.265	-0.683	-0.001	0.596	0.044	0.319	-0.130
0.015	0.000	-0.019	0.014	0.000	-0.043	0.696	0.266	0.000	0.570	-0.319	-0.049	0.131
0.086	0.000	0.019	-0.019	0.000	-0.066	0.404	-0.418	0.000	-0.519	-0.343	0.348	-0.003
0.011	0.000	0.015	0.118	0.000	-0.028	0.532	0.052	0.000	-0.194	0.831	0.127	-0.084
-0.011	0.000	0.118	0.015	0.000	0.028	0.063	0.536	0.000	0.182	0.130	0.828	-0.085

H

1.000	0.000	0.012	0.015	0.036	0.012	0.121	0.000
0.000	0.964	0.000	0.000	0.000	0.000	0.000	-0.035
0.016	0.000	0.817	0.670	-0.055	0.281	-0.076	0.000
-0.033	0.000	-0.300	0.676	-0.621	0.131	0.031	0.000
0.092	0.000	-0.003	-0.030	-0.442	-0.017	0.883	0.000

2×Li

0.999	0.000	0.087	-0.087
0.000	0.999	0.000	0.000
0.000	0.000	0.837	0.837
0.111	0.000	0.466	-0.466

Table S9

Non-trivial pDAFH and DAFH eigenvalues for selected domains in Li_4. The upper row corresponds to pDAFH and the lower one to DAFH analysis.

Domain	ε_1	ε_2	ε_3	ε_4	ε_5	ε_6	ε_7	ε_8	ε_9	ε_{10}
Li_1	0.079	0.079	0.004	0.003						
	0.084	0.084	0.003	0.003	0.003	0.003				
Li_3	0.363	0.013	0.011	0.009						
	0.363	0.027	0.016	0.009	0.005	0.001				
NNA_2	1.238	0.077	0.058	0.037	0.020	0.002	0.002	0.001		
	1.232	0.062	0.051	0.044	0.033	0.007	0.005	0.002	0.002	0.002

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Table S10

Overlap integrals between pDAFH and DAFH functions for Li_4. For each of the selected domains, the rows correspond to the different pDAFH functions and the columns to the different DAFH functions for the same domain, always in strict order of decreasing eigenvalue.

Li_1

0.997	0.365	0.086	-0.050	0.000	0.000
0.365	0.997	-0.049	0.085	0.000	0.000
0.069	0.069	0.750	0.749	0.000	0.000
0.000	0.000	0.000	0.000	0.778	0.778

Li_3

0.999	0.000	0.226	0.000	0.000	-0.010
0.000	0.990	0.000	0.000	0.027	0.000
0.108	0.000	0.576	0.000	0.000	-0.416
0.000	0.000	0.000	0.980	0.000	0.000

NNA_2

1.000	0.000	0.055	-0.100	0.000	0.000	-0.017	-0.096	0.006	0.000
0.000	1.000	0.000	0.000	0.000	0.058	0.000	0.000	0.000	0.000
0.005	0.000	0.957	0.561	0.000	0.000	0.124	-0.092	-0.192	0.000
0.000	0.000	0.000	0.000	1.000	0.000	0.000	0.000	0.000	-0.128
-0.092	0.000	0.170	0.942	0.000	0.000	-0.294	-0.139	-0.117	0.000
0.000	0.000	0.000	0.000	-0.128	0.000	0.000	0.000	0.000	1.000
-0.155	0.000	-0.046	-0.087	0.000	0.000	-0.041	0.964	-0.056	0.000
-0.093	0.000	0.171	0.364	0.000	0.000	0.903	0.067	0.086	0.000

Appendix S1: Analysis of minimal basis full CI calculations for H_2

A full CI calculation for H_2 in a minimal basis set generates two orthonormal natural orbitals, $1\sigma_g$ and $1\sigma_u$, with occupancies n_1 and $n_2=2-n_1$, respectively. We consider the domain of one of the H atoms, for which we can write the AOM matrix in the form:

$$\mathbf{a}^{\Omega} = \begin{pmatrix} ½ & t \\ t & ½ \end{pmatrix} \tag{S1.1}$$

in which the value of the off-diagonal elements t varies with the bond length, R. The corresponding AOM matrix for the domain of the other H atom is of course identical, except for the phase of the off-diagonal elements, so that the sum of the two AOM matrices is a unit matrix.

The nonzero elements of the two-electron density matrix **D2** expressed in this natural orbital basis are:

$$\begin{aligned} &\mathrm{D2}(1\ 1|1\ 1) = ½n_1 \\ &\mathrm{D2}(2\ 2|1\ 1) = \mathrm{D2}(1\ 1|2\ 2) = -½\sqrt{n_1 n_2} \\ &\mathrm{D2}(2\ 2|2\ 2) = ½n_2 \end{aligned} \tag{S1.2}$$

in which the relevant indices have been written in the standard order that is used with bra-ket notation.

Recalling that the corresponding one-electron density matrix is diagonal, with elements n_1 and n_2, and that the integral of the total electron density over the domain of either H atom must be unity, substitution into eqn (2.2) in the paper leads us to:

$$\mathbf{G}^{\Omega} = \begin{pmatrix} ½n_1 & t\sqrt{n_1 n_2} \\ t\sqrt{n_1 n_2} & ½n_2 \end{pmatrix} \tag{S1.3}$$

It is useful to observe for the special case of the minimal basis full CI treatment of H_2 that the matrix $\mathbf{n}^{½}\mathbf{a}^{\Omega}\mathbf{n}^{½}$, which is diagonalized in the pDAFH approach (see eqn (2.9) in the paper), coincides with the matrix $\mathbf{G}^{\Omega}$ in eqn (S1.3) that is diagonalized in the full DAFH approach. Defining

$$r = \sqrt{¼ + n_1(2-n_1)(t^2-¼)} \tag{S1.4}$$

the expressions for the the eigenvalues λ_i and eigenvectors $\mathbf{v}_i$ of this matrix can be written for $0 < n_1 < 2$ in the form:

$$\lambda_1 = ½+r \qquad \mathbf{v}_1 = \begin{pmatrix} \dfrac{t\sqrt{n_1(2-n_1)}}{\sqrt{t^2 n_1(2-n_1) + (-½n_1+½+r)^2}} \\ \dfrac{(-½n_1+½+r)}{\sqrt{t^2 n_1(2-n_1) + (-½n_1+½+r)^2}} \end{pmatrix} \tag{S1.5}$$

and

$$\lambda_2 = \tfrac{1}{2}-r \qquad \mathbf{v}_2 = \begin{pmatrix} \dfrac{t\sqrt{n_1(2-n_1)}}{\sqrt{t^2 n_1(2-n_1) + (-\tfrac{1}{2}n_1+\tfrac{1}{2}-r)^2}} \\ \dfrac{(-\tfrac{1}{2}n_1+\tfrac{1}{2}-r)}{\sqrt{t^2 n_1(2-n_1) + (-\tfrac{1}{2}n_1+\tfrac{1}{2}-r)^2}} \end{pmatrix} \tag{S1.6}$$

It is useful to consider briefly two limiting cases. As n_1 approaches unity, as occurs for large R, $\mathbf{v}_1$ tends to $\sqrt{\tfrac{1}{2}}(1\sigma_g+1\sigma_u)$, which is a function localized on one H atom and, as t tends to ½, λ_1 tends to unity. Similarly, $\mathbf{v}_2$ tends to $\sqrt{\tfrac{1}{2}}(1\sigma_g-1\sigma_u)$, which is localized on the other H atom and, as t tends to ½, λ_2 tends to zero. On the other hand, for n_1 approaching two, as could be appropriate for very small R, λ_1 tends to unity and $\mathbf{v}_1$ to $1\sigma_g$, whereas λ_2 tends to zero.

All of the analysis presented here was confirmed numerically for a few different bond lengths using full CI calculations for H_2 with a STO-3G basis.