Supporting Information for

Diabatic-At-Construction (DAC) Method for Diabatic and Adiabatic Ground and Excited States Based on Multistate Density Functional Theory

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1. *Optimization of Block-Localized Kohn-Sham Orbitals*

We partition a system consisting of *N* electrons and *M* basis functions into *K* blocks with n_A electrons and m_A basis functions in block *A*. The block-localized Kohn-Sham (BLKS) orbitals corresponding to a given charge and spin character,[1-3] are written in terms of the atomic orbitals located on atoms in the particular subspace:

$$|\psi_i^A>=\boldsymbol{\chi}_A\mathbf{C}_i^A=\sum_{\mu=1}^{m_A}|\chi_{A\mu}>c_{\mu i}^A,\quad A=1,\cdots,K \tag{A1}$$

where $c_{\mu i}^A$ is an element of the column coefficient vector ($\mathbf{C}_i^A$) of KS orbital *i* ($|\psi_i^A>$), and $\{|\chi_{A\mu}>\}_{\mu=1}^{m_A}$ are the basis functions in block *A*, arranged as a row vector $\boldsymbol{\chi}_A$. Let $\Omega^A=\psi_1^A\alpha\psi_1^A\beta\cdots\psi_{n_A/2}^A\beta$ be a successive product of n_A occupied spin-orbitals in block *A*, and α and β are spin functions. The Slater determinant function for the block-localized system is constructed as follows:

$$\Phi=\frac{1}{\sqrt{N!}}\hat{A}\{\Omega^1\Omega^2\cdots\Omega^K\} \tag{A2}$$

where $\hat{A}$ is an antisymmetrization operator.

The overlap matrix of the MOs is given as follows

$$\mathbf{S}=\mathbf{C}^{\mathbf{T}}\mathbf{R}\mathbf{C} \tag{A3}$$

where $\mathbf{R}=\boldsymbol{\chi}^T\boldsymbol{\chi}$ is the overlap in terms of the basis functions, and $\mathbf{C}$ is the transformation matrix. The one-particle density matrix from the occupied nonorthogonal BLKS orbitals is

$$\mathbf{D} = \mathbf{C}(\mathbf{C}^T\mathbf{R}\mathbf{C})^{-1}\mathbf{C}^T \quad \text{(A4)}$$

which satisfies the symmetry ($\mathbf{D}^T = \mathbf{D}$), rank ($Tr(\mathbf{DR}) = N$) and idempotency ($\mathbf{DRD} = \mathbf{D}$) conditions, and the electron density is given as follows

$$\rho(\mathbf{r}) = \sum_{\mu\nu}^{m} |\, \chi_\mu(\mathbf{r}) > D_{\mu\nu} < \chi_\nu(\mathbf{r}) \,| = \boldsymbol{\chi}(\mathbf{r})\mathbf{D}\boldsymbol{\chi}^{\mathbf{T}}(\mathbf{r}) \quad \text{(A5)}$$

Using the one-particle density, we obtain the BLDFT energy as:[1]

$$E[\rho] = Tr(\mathbf{Dh}) + \frac{1}{2}Tr(\mathbf{DJD}) + E_{xc}[\rho(\mathbf{r})] + E_{nuc} \quad \text{(A6)}$$

where E_{nuc} is the coulomb energy of the nuclei, $\mathbf{h}$ and $\mathbf{J}$ are the usual Hamiltonian (one-electron) and Coulomb integral matrices, and $E_{xc}[\rho(\mathbf{r})]$ is the exchange-correlation energy functional.

The block-localized Kohn-Sham equations for the nonorthogonal KS orbitals can be derived.[1,3-10] Because the coefficient matrix is block-diagonal, the conventional SCF procedure for the Kohn-Sham equations of the entire system can be cast into *K* separate KS equations, one set for each subgroup. First, define a projection operator $\hat{P}_{\notin A}$, excluding orbitals in block *A*, indicated by the subscripts $\notin A$:

$$\hat{P}_{\notin A} = \sum_{B,C\neq A}^{K} \sum_{i,j}^{occ} |\, \psi_i^B > [(\mathbf{S}_{\notin A})^{-1}]_{ij} < \psi_j^C \,| \quad \text{(A7)}$$

where $\mathbf{S}_{\notin A}$ is the overlap matrix without the occupied KS orbitals of block *A*. Then, the KS equations for the orbitals of block *A* are

$$\hat{F}^A \,|\, \psi_i^A > = (\hat{1} - \hat{P}_{\notin A})\hat{F}(\hat{1} - \hat{P}_{\notin A}) \,|\, \psi_i^A > = (\hat{1} - \hat{P}_{\notin A}) \,|\, \psi_i^A > \varepsilon_i^A \quad \text{(A8)}$$

with $\hat{F}$ being the unprojected (conventional) KS operator. In matrix form in terms of the basis functions, the generalized secular equations can be written as follows:[3,9,10]

$$\mathbf{F}_{AA}^{P}\mathbf{C}_{AA} = \mathbf{R}_{AA}^{P}\mathbf{C}_{AA}\boldsymbol{\varepsilon}_{AA} \quad \text{(A9)}$$

where $\boldsymbol{\varepsilon}_{AA}$ is a diagonal matrix corresponding to orbital energies, and the projected overlap ($\mathbf{R}_{AA}^{P}$) and KS-Fock ($\mathbf{F}_{AA}^{P}$) matrices are given as

$$\mathbf{R}_{AA}^{P} = (\mathbf{R}_{AA}, \mathbf{R}_{AB})\mathbf{P}_{\notin A} \quad \text{(A10)}$$

$$\mathbf{F}_{AA}^{P} = (\mathbf{P}_{\notin A})^{T}\mathbf{F}\mathbf{P}_{\notin A} \quad \text{(A11)}$$

The projection matrix is defined by

$$\mathbf{P}_{\notin A} = \begin{pmatrix} \mathbf{1}_{AA} \\ -\mathbf{D}_{BB}\mathbf{R}_{BA} \end{pmatrix} \quad \text{(A12)}$$

where the subscripts specifies the corresponding block matrices.

The computational procedure is conveniently described by considering an effective partition of two blocks, *A* and *B*, where the orbitals in *A* are being optimized. Starting from an initial guess, one iteratively optimizes the KS orbitals of each block employing the densities generated previously for other blocks until the total energy and density are converged.

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2. *Numerical data for Figure 1*.

Relative energies (eV) of singlet states of LiH as a function of Li-H distance from MS-CASPT2/SA(4)-CASSCF/aug-cc-pVTZ calculations

R(H-Li), Å	X(S0)	A(S1)	C(S2)	D(S3)
0.95252	0.90600	4.61993	7.09820	7.50061
1.05835	-0.44458	3.40487	5.80424	6.22618
1.19065	-1.49537	2.39233	4.73380	5.16477
1.32294	-2.07747	1.75075	4.06676	4.49464
1.45524	-2.35935	1.34709	3.66013	4.07724
1.58753	-2.44945	1.09655	3.42135	3.82365
1.71983	-2.41837	0.94502	3.28965	3.67621
1.85212	-2.31265	0.85782	3.22472	3.59714
1.98441	-2.16322	0.81221	3.19995	3.56156
2.11671	-1.99037	0.79252	3.19809	3.55301
2.24900	-1.80714	0.78782	3.20811	3.56066
2.38130	-1.62177	0.79099	3.22296	3.57729
2.51359	-1.43954	0.79822	3.23807	3.59825
2.64589	-1.26396	0.80821	3.25039	3.62078
2.91047	-0.94203	0.83774	3.25868	3.66674
3.17506	-0.66937	0.88548	3.23612	3.71624
3.43965	-0.45331	0.95551	3.18018	3.76872
3.70424	-0.29537	1.03948	3.09602	3.78348
3.96883	-0.18759	1.12445	2.98835	3.73239
4.23342	-0.11742	1.22288	2.88905	3.68393
4.49801	-0.07427	1.33414	2.82036	3.65792
4.76260	-0.04863	1.44493	2.78062	3.64371
5.29177	-0.02462	1.62693	2.76375	3.62525
5.82095	-0.01605	1.73884	2.80198	3.60611
6.35013	-0.01266	1.79598	2.87296	3.58421
7.93766	-0.00924	1.83723	3.15986	3.57071
9.00000	-0.00791	1.83999	3.27926	3.64115
10.58354	-0.00499	1.84092	3.32893	3.75158
12.00000	-0.00254	1.84116	3.33717	3.79180
15.87532	-0.00100	1.84107	3.33981	3.80675

Relative energies (eV) as a function of Li-H distance from MSDFT/PBE0/aug-cc-pVTZ calculations.

R(H-Li), Å	X(S0)	A(S1)	C(S2)	D(S3)
1.0000	0.6054	4.3469	6.9654	7.3609
1.1000	-0.5210	3.3047	5.8501	6.2813
1.2000	-1.2691	2.5628	5.0743	5.5136
1.3000	-1.7437	2.0294	4.5453	4.9664
1.4000	-2.0247	1.6447	4.1943	4.5792
1.5000	-2.1707	1.3703	3.9686	4.3127

1.6000	-2.2227	1.1797	3.8283	4.1383
1.7000	-2.2095	1.0462	3.7448	4.0352
1.8000	-2.1520	0.9479	3.6968	3.9855
1.9000	-2.0646	0.8723	3.6707	3.9722
2.0000	-1.9575	0.8138	3.6590	3.9779
2.1250	-1.8071	0.7609	3.6582	3.9865
2.2500	-1.6478	0.7268	3.6674	3.9731
2.5000	-1.3282	0.6992	3.6929	3.8526
2.6250	-1.1753	0.6997	3.6809	3.7845
2.7500	-1.0299	0.7072	3.6114	3.7678
2.8750	-0.8932	0.7205	3.5228	3.7727
3.0000	-0.7662	0.7389	3.4384	3.7779
3.1250	-0.6495	0.7621	3.3569	3.7791
3.2500	-0.5439	0.7901	3.2789	3.7746
3.3750	-0.4502	0.8224	3.2047	3.7649
3.5000	-0.3684	0.8591	3.1305	3.7511
3.7500	-0.2396	0.9445	2.9825	3.7190
4.0000	-0.1512	1.0419	2.8466	3.6899
4.5000	-0.0573	1.2445	2.6477	3.6485
5.0000	-0.0215	1.4158	2.5548	3.6206
6.0000	-0.0036	1.5955	2.6138	3.5833
8.0000	-0.0010	1.6481	3.0415	3.5419
10.0000	-0.0009	1.6499	3.4025	3.5346
12.0000	-0.0009	1.6499	3.4909	3.7022

3. *Numerical data for Figure 2*.

Relative energies (eV) of triplet states of LiH as a function of interatomic distance from MS-CASPT2/SA(4)-CASSCF/aug-cc-pVTZ calculations

R(H-Li), Å	a(T1)	c(T2)	d(T3)
0.9525	4.3651	6.8277	7.4325
1.0584	3.1522	5.5363	6.1523
1.1906	2.1369	4.4698	5.0768
1.3229	1.4876	3.8112	4.3884
1.4552	1.0715	3.4131	3.9564
1.5875	0.8030	3.1812	3.6840
1.7198	0.6272	3.0557	3.5057
1.8521	0.5085	2.9966	3.3697
1.9844	0.4252	2.9802	3.2423
2.1167	0.3615	2.9579	3.1344
2.2490	0.3104	2.8722	3.1032
2.3813	0.2626	2.7408	3.1524
2.5136	0.2252	2.6184	3.1864
2.6459	0.1921	2.5119	3.2203
2.9105	0.1371	2.3378	3.2788
3.1751	0.0952	2.2096	3.3208
3.4397	0.0649	2.1177	3.3488
3.7042	0.0440	2.0529	3.3668
3.9688	0.0300	2.0081	3.3783
4.2334	0.0208	1.9775	3.3857

Relative energies (eV) of triplet states of LiH as a function of interatomic distance from MSDFT/PBE0/aug-cc-pVTZ calculations

R(H-Li), Å	a(T1)	C(T2)	d(T3)	e(T4)
0.9000	5.4286	8.2744	8.8878	16.0053
1.0000	4.0009	6.6845	7.3672	14.0891
1.1000	3.0054	5.5511	6.3021	12.9002
1.2000	2.3122	4.7484	5.5496	12.2260
1.3000	1.8271	4.1858	5.0138	11.8210
1.4000	1.4808	3.7977	4.6308	11.3793
1.5000	1.2227	3.5404	4.3597	10.5653
1.6000	1.0214	3.3809	4.1698	9.2816
1.7000	0.8577	3.2945	4.0369	7.8236
1.8000	0.7196	3.2614	3.9382	6.5428
1.9000	0.6009	3.2651	3.8478	5.5738
2.0000	0.4998	3.2927	3.7305	4.9153
2.1250	0.3972	3.3432	3.4937	4.4727
2.2500	0.3181	3.1806	3.4138	4.3025

2.5000	0.2108	2.6761	3.5311	4.1865
2.6250	0.1739	2.4968	3.5820	4.1377
2.7500	0.1442	2.3550	3.6260	4.0793
2.8750	0.1198	2.2414	3.6631	4.0135
3.0000	0.0995	2.1489	3.6933	3.9453
3.1250	0.0825	2.0722	3.7153	3.8793
3.2500	0.0681	2.0080	3.7214	3.8328
3.3750	0.0561	1.9535	3.7025	3.8249
3.5000	0.0461	1.9068	3.6736	3.8382
3.7500	0.0308	1.8328	3.6268	3.8777
4.0000	0.0202	1.7791	3.5976	3.9163
4.5000	0.0081	1.7134	3.5647	3.9736
5.0000	0.0028	1.6810	3.5448	3.9987
6.0000	-0.0004	1.6577	3.5196	3.9764
8.0000	-0.0009	1.6504	3.4976	3.8739
10.0000	-0.0009	1.6499	3.4932	3.8321
12.0000	-0.0009	1.6499	3.4928	3.8239

4. *Numerical data for Figure 3*.

Relative energies (eV) for the VDC states of singlet LiH as a function of interatomic distance from BL-KSDFT and MSDFT/PBE0/aug-cc-pVTZ calculations

R(Å)	ionic	S(2s-1s)	S(3s-1s)	S(2p-1s)	S(3p-1s)
0.9000	2.9153	3.4481	8.5053	3.8101	24.1895
1.0000	1.1326	1.6992	6.9184	2.3548	7.0829
1.1000	-0.1028	0.4612	5.8274	1.3396	6.0092
1.2000	-0.9336	-0.3881	5.0995	0.6594	5.2506
1.3000	-1.4695	-0.9480	4.6354	0.2151	4.7163
1.4000	-1.7931	-1.2991	4.3626	-0.0619	4.3425
1.5000	-1.9650	-1.5043	4.2115	-0.2204	4.0837
1.6000	-2.0292	-1.6085	4.1323	-0.2952	3.9080
1.7000	-2.0171	-1.6414	4.0828	-0.3114	3.7923
1.8000	-1.9507	-1.6219	4.0228	-0.2871	3.7200
1.9000	-1.8454	-1.5629	3.9218	-0.2354	3.6788
2.0000	-1.7122	-1.4753	3.7723	-0.1651	3.6598
2.1250	-1.5182	-1.3406	3.5380	-0.0609	3.6572
2.2500	-1.3043	-1.1927	3.2980	0.0538	3.6690
2.5000	-0.8495	-0.8973	2.9421	0.2943	3.7112
2.6250	-0.6209	-0.7606	2.8464	0.4137	3.7334
2.7500	-0.3974	-0.6351	2.8014	0.5298	3.7532
2.8750	-0.1822	-0.5228	2.7991	0.6411	3.7690
3.0000	0.0229	-0.4250	2.8308	0.7464	3.7804
3.1250	0.2168	-0.3417	2.8896	0.8451	3.7868
3.2500	0.3991	-0.2729	2.9605	0.9368	3.7884
3.3750	0.5701	-0.2172	3.0266	1.0212	3.7857
3.5000	0.7301	-0.1726	3.0839	1.0984	3.7791
3.7500	1.0198	-0.1082	3.1703	1.2315	3.8196
4.0000	1.2741	-0.0672	3.2277	1.3383	3.7267
4.5000	1.6972	-0.0252	3.3001	1.4859	3.6643
5.0000	2.0339	-0.0090	3.3503	1.5686	3.6216
6.0000	2.5345	-0.0009	3.4226	1.6324	3.6186
8.0000	3.1501	0.0001	3.4836	1.6494	3.7405
10.0000	3.5145	0.0001	3.4923	1.6499	3.8076
12.0000	3.7560	0.0002	3.4928	1.6499	3.8214

5. *Numerical data for Figure 4*.

Relative energies (eV) for the Gram-Schmidt orthogonalized DAC diabatic states of singlet LiH as a function of interatomic distance from BL-KSDFT and MSDFT/PBE0/aug-cc-pVTZ calculations.

4(a) direct GS orthogonalization.

R(Å)	ionic	2s	3s	2p	3p
1.0000	1.1325	8.1718	7.3783	22.8611	7.3075
1.1000	-0.1028	7.7089	6.3405	22.1642	6.1745
1.2000	-0.9336	7.5581	5.6556	22.3628	5.3570
1.3000	-1.4696	7.4727	5.1968	23.1411	4.8038
1.4000	-1.7929	7.2281	4.8466	23.9103	4.4781
1.5000	-1.9649	6.6849	4.5383	23.8431	4.3040
1.6000	-2.0291	5.8651	4.2702	22.3993	4.1690
1.7000	-2.0171	4.9307	4.0871	19.8191	4.0153
1.8000	-1.9507	4.0594	4.0126	16.8567	3.8689
1.9000	-1.8454	3.3508	4.0245	14.1261	3.7652
2.0000	-1.7121	2.8204	4.0879	11.8738	3.7075
2.1250	-1.5181	2.3581	4.1919	9.7326	3.6825
2.2500	-1.3042	2.0414	4.2833	8.1796	3.6906
2.5000	-0.8495	1.6153	4.3233	6.1464	3.7687
2.6250	-0.6209	1.4487	4.2645	5.4379	3.8229
2.7500	-0.3975	1.2983	4.1745	4.8558	3.8760
2.8750	-0.1823	1.1595	4.0762	4.3736	3.9219
3.0000	0.0229	1.0310	3.9862	3.9750	3.9589
3.1250	0.2169	0.9124	3.9034	3.6539	3.9883
3.2500	0.3992	0.8046	3.8365	3.3930	4.0128
3.3750	0.5701	0.7083	3.7935	3.1723	4.0357
3.5000	0.7301	0.6221	3.7655	2.9856	4.0575
3.7500	1.0199	0.4770	3.7355	2.6893	4.1002
4.0000	1.2740	0.3627	3.7230	2.4656	4.1404
4.5000	1.6972	0.2044	3.7119	2.1538	4.2060
5.0000	2.0340	0.1116	3.6955	1.9570	4.2425
6.0000	2.5345	0.0302	3.6392	1.7568	4.2213
8.0000	3.1500	0.0017	3.5350	1.6596	4.0166
10.0000	3.5143	0.0000	3.4994	1.6506	3.8795
12.0000	3.7560	0.0000	3.4934	1.6501	3.8335

4(b) an equal mixture of $2s$ and $2p$ states of Li, $\Psi'_{2s} = N_b(\Psi_{2s} + \Psi_{2p})$ and $\Psi'_{2p} = N_b(\Psi_{2p} - \Psi_{2s})$, where N_b is a normalization factor.

R(Å)	ionic	2s	3s	2p	3p
1.0000	1.1325	4.4471	7.1854	26.7786	7.3075
1.1000	-0.1028	3.4588	6.0800	26.6750	6.1745
1.2000	-0.9336	2.7608	5.3217	27.4940	5.3570
1.3000	-1.4696	2.2585	4.8117	28.7403	4.8038
1.4000	-1.7929	1.8863	4.4768	29.6219	4.4781
1.5000	-1.9649	1.6008	4.2623	29.2031	4.3040
1.6000	-2.0291	1.3755	4.1287	27.0301	4.1690
1.7000	-2.0171	1.1946	4.0504	23.5917	4.0153
1.8000	-1.9507	1.0495	4.0104	19.8684	3.8689
1.9000	-1.8454	0.9361	3.9938	16.5718	3.7652
2.0000	-1.7121	0.8504	3.9867	13.9454	3.7075
2.1250	-1.5181	0.7761	3.9696	11.5372	3.6825
2.2500	-1.3042	0.7298	3.9247	9.8496	3.6906
2.5000	-0.8495	0.6868	3.7396	7.6583	3.7687
2.6250	-0.6209	0.6776	3.6281	6.8458	3.8229
2.7500	-0.3975	0.6721	3.5298	6.1263	3.8760
2.8750	-0.1823	0.6691	3.4610	5.4790	3.9219
3.0000	0.0229	0.6683	3.4262	4.8977	3.9589
3.1250	0.2169	0.6694	3.4158	4.3845	3.9883
3.2500	0.3992	0.6732	3.4234	3.9372	4.0128
3.3750	0.5701	0.6797	3.4455	3.5489	4.0357
3.5000	0.7301	0.6882	3.4727	3.2125	4.0575
3.7500	1.0199	0.7089	3.5274	2.6656	4.1002
4.0000	1.2740	0.7314	3.5745	2.2455	4.1404
4.5000	1.6972	0.7709	3.6389	1.6602	4.2060
5.0000	2.0340	0.7973	3.6632	1.3040	4.2425
6.0000	2.5345	0.8199	3.6346	0.9717	4.2213
8.0000	3.1500	0.8256	3.5350	0.8357	4.0166
10.0000	3.5143	0.8251	3.4994	0.8256	3.8795
12.0000	3.7560	0.8251	3.4934	0.8251	3.8335

4(c) the same *sp*-mixing as in (b) scaled by the overlap integral,
$\Psi'_{2s} = N_c(\Psi_{2s} + S_{2s2p}\Psi_{2p})$ and $\Psi'_{2p} = N'_c(\Psi_{2p} - S_{2s2p}\Psi_{2s})$.

R(Å)	ionic	2s	3s	2p	3p
1.0000	1.1325	4.5108	7.2052	26.6948	7.3075
1.1000	-0.1028	3.5187	6.1010	26.5941	6.1745
1.2000	-0.9336	2.8128	5.3413	27.4224	5.3570
1.3000	-1.4696	2.3002	4.8286	28.6820	4.8038
1.4000	-1.7929	1.9176	4.4898	29.5776	4.4781
1.5000	-1.9649	1.6237	4.2716	29.1710	4.3040
1.6000	-2.0291	1.3913	4.1339	27.0091	4.1690
1.7000	-2.0171	1.2041	4.0512	23.5816	4.0153
1.8000	-1.9507	1.0542	4.0066	19.8676	3.8689
1.9000	-1.8454	0.9377	3.9878	16.5759	3.7652
2.0000	-1.7121	0.8525	3.9840	13.9457	3.7075
2.1250	-1.5181	0.7840	3.9845	11.5144	3.6825
2.2500	-1.3042	0.7464	3.9766	9.7810	3.6906
2.5000	-0.8495	0.7151	3.9100	7.4599	3.7687
2.6250	-0.6209	0.7023	3.8596	6.5892	3.8229
2.7500	-0.3975	0.6844	3.8101	5.8338	3.8760
2.8750	-0.1823	0.6588	3.7704	5.1802	3.9219
3.0000	0.0229	0.6256	3.7423	4.6243	3.9589
3.1250	0.2169	0.5859	3.7168	4.1671	3.9883
3.2500	0.3992	0.5423	3.6958	3.7957	4.0128
3.3750	0.5701	0.4974	3.6871	3.4893	4.0357
3.5000	0.7301	0.4528	3.6847	3.2360	4.0575
3.7500	1.0199	0.3685	3.6871	2.8463	4.1002
4.0000	1.2740	0.2936	3.6934	2.5644	4.1404
4.5000	1.6972	0.1774	3.7007	2.1921	4.2060
5.0000	2.0340	0.1015	3.6917	1.9712	4.2425
6.0000	2.5345	0.0291	3.6387	1.7581	4.2213
8.0000	3.1500	0.0017	3.5350	1.6596	4.0166
10.0000	3.5143	0.0000	3.4994	1.6506	3.8795
12.0000	3.7560	0.0000	3.4934	1.6501	3.8335

4.(d) the inclusion of a small amount (25%) of the 2*s*-covalent state (also overlap-dependent) in the ionic configuration, $\Psi'_{2s} = N_c(\Psi_{2s} + S_{2s2p}\Psi_{2p})$

$\Psi'_{2p} = N'_c(\Psi_{2p} - S_{2s2p}\Psi_{2s})$, and $\Psi'_{\text{ion}} = N_d(\Psi_{\text{ion}} + 0.25S_{2s2p}\Psi_{2s})$.

R(Å)	ionic	2s	3s	2p	3p
1.0000	1.3342	4.6202	7.2188	26.3705	7.3075
1.1000	0.0879	3.6196	6.1173	26.2861	6.1745
1.2000	-0.7573	2.9056	5.3592	27.1354	5.3570
1.3000	-1.3086	2.3826	4.8463	28.4208	4.8038
1.4000	-1.6435	1.9870	4.5051	29.3435	4.4781
1.5000	-1.8185	1.6762	4.2830	28.9607	4.3040
1.6000	-1.8759	1.4240	4.1407	26.8162	4.1690
1.7000	-1.8484	1.2147	4.0536	23.3996	4.0153
1.8000	-1.7622	1.0417	4.0063	19.6921	3.8689
1.9000	-1.6375	0.9026	3.9875	16.4036	3.7652
2.0000	-1.4882	0.7970	3.9867	13.7745	3.7075
2.1250	-1.2805	0.7075	3.9957	11.3421	3.6825
2.2500	-1.0596	0.6534	3.9984	9.6074	3.6906
2.5000	-0.6024	0.5954	3.9494	7.2928	3.7687
2.6250	-0.3769	0.5717	3.9023	6.4332	3.8229
2.7500	-0.1594	0.5448	3.8520	5.6936	3.8760
2.8750	0.0474	0.5135	3.8082	5.0583	3.9219
3.0000	0.2408	0.4784	3.7742	4.5217	3.9589
3.1250	0.4210	0.4406	3.7421	4.0828	3.9883
3.2500	0.5878	0.4022	3.7154	3.7277	4.0128
3.3750	0.7423	0.3652	3.7023	3.4343	4.0357
3.5000	0.8855	0.3301	3.6961	3.1916	4.0575
3.7500	1.1434	0.2664	3.6942	2.8177	4.1002
4.0000	1.3701	0.2117	3.6977	2.5459	4.1404
4.5000	1.7524	0.1282	3.7023	2.1845	4.2060
5.0000	2.0642	0.0735	3.6923	1.9682	4.2425
6.0000	2.5429	0.0212	3.6389	1.7578	4.2213
8.0000	3.1505	0.0011	3.5350	1.6596	4.0166
10.0000	3.5146	0.0000	3.4994	1.6506	3.8795
12.0000	3.7560	0.0000	3.4934	1.6501	3.8335

6. *Numerical data for Figure 5.*

Selected computed diabatic coupling (eV) for the Gram-Schmidt orthogonalized DAC diabatic states in 4(d) above as a function of interatomic distance from MSDFT/PBE0/aug-cc-pVTZ calculations.

R(A)	ionic-2s	ionic-3s	ionic-2p	ionic-3p	2s-3s	2p-3p	2s-2p	3s-3p
1.000	0.000093	0.016323	14.17469	0.303449	0.448542	3.246486	1.879847	0.004553
1.100	0.000796	0.016837	11.94907	0.202685	0.492659	1.925263	2.073902	0.012261
1.200	0.002213	0.012799	10.30408	0.112665	0.491257	0.548205	2.216272	0.026991
1.300	0.003550	0.008089	9.020544	0.048052	0.447702	0.018131	2.195879	0.049512
1.400	0.006631	0.005401	7.992775	0.012659	0.370254	1.230299	1.957237	0.073589
1.500	0.015265	0.005617	7.173206	0.000848	0.280057	3.475228	1.534722	0.085554
1.600	0.035501	0.009746	6.508464	0.000449	0.189226	4.378597	1.068513	0.075813
1.700	0.073148	0.020005	5.924725	0.001407	0.108346	3.271027	0.702744	0.052019
1.800	0.129398	0.038199	5.369223	0.000868	0.047229	1.723133	0.485310	0.029252
1.900	0.198906	0.064084	4.833695	0.000112	0.010979	0.761137	0.386853	0.014007
2.000	0.272869	0.095887	4.339451	0.000079	0.000012	0.344089	0.364101	0.005324
2.125	0.360906	0.140657	3.813800	0.000745	0.015601	0.182562	0.394623	0.000464
2.250	0.439079	0.185844	3.400060	0.001494	0.050018	0.167272	0.450846	0.000935
2.500	0.568303	0.244530	2.827555	0.002617	0.118798	0.270990	0.515988	0.018931
2.625	0.620259	0.243639	2.617478	0.003215	0.139086	0.323038	0.494132	0.033136
2.750	0.661454	0.221794	2.432171	0.003916	0.148446	0.345791	0.439901	0.045701
2.875	0.689158	0.185541	2.259324	0.004609	0.148071	0.338067	0.367544	0.054143
3.000	0.701613	0.143890	2.091743	0.005101	0.139409	0.310619	0.291517	0.058296
3.125	0.698570	0.105526	1.926094	0.005142	0.123833	0.276950	0.222437	0.058968
3.250	0.681630	0.073769	1.763862	0.004672	0.105393	0.245192	0.165414	0.058399
3.375	0.653722	0.048276	1.608745	0.003819	0.088378	0.218108	0.120768	0.058776
3.500	0.617884	0.029299	1.462106	0.002729	0.073528	0.195761	0.086862	0.060034
3.750	0.533531	0.007363	1.198638	0.000664	0.050724	0.161537	0.043084	0.064536
4.000	0.445381	0.000202	0.976240	0.000068	0.035170	0.135330	0.020010	0.070312
4.500	0.289635	0.009162	0.638857	0.007683	0.016689	0.092634	0.003141	0.079443
5.000	0.176413	0.027917	0.410255	0.027781	0.007509	0.057961	0.000150	0.079349
6.000	0.056561	0.049038	0.157866	0.076477	0.001268	0.015899	0.000221	0.053815
8.000	0.003507	0.025993	0.017171	0.080155	0.000017	0.000179	0.000059	0.007559
10.00	0.000120	0.005353	0.001222	0.031950	0.000000	0.000081	0.000002	0.000339
12.00	0.000002	0.000624	0.000060	0.007434	0.000000	0.000140	0.000000	0.000006