Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Ab-initio Methodologies for Prediction of Bridge-Mediated Electronic Coupling: Through Space and Through Bond Interactions.

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ABSTRACT: A Density Functional Theory-based Green's Function Pathway Model is developed enabling further advancements towards the long-standing challenge of accurate yet inexpensive prediction of electron transfer rate. Electronic coupling predictions are demonstrated to within 0.1 eV of experiment for organic and biological systems of moderately large size, with modest computational expense. Benchmarking and comparisons are made across density functional type, basis set extent, and orbital localization scheme. The resulting framework is shown to be flexible and to offer quantitative prediction of both electronic coupling and tunneling pathways in covalently bound non-adiabatic donor-bridge-acceptor (D-B-A) systems. A new LMO-GFM Pathways adaptation enables a more intuitive understanding of electron tunneling in terms of through-bond and through-space interactions.

Electronic Supplementary Information

Table S1. Basis set study of effective Hamiltonian predictions of T_{DA} with B97-D, as a function of basis set for Set A molecules **1-5.**

	$\|T_{DA}\|$ (eV)				
	Molecule				
Method/Basis:	**5**	**4**	**3**	**2**	**1**
B97-D/STO-3G	0.0126	0.0458	0.0575	0.1732	0.4445
B97-D /STO-6G	0.0127	0.0468	0.0574	0.1744	0.4417
B97-D /Def2-SVP	0.0224	0.0419	0.0748	0.1718	0.5469
B97-D /3-21G	0.0214	0.0475	0.0692	0.1719	0.4771
B97-D /6-31G	0.0209	0.0509	0.0692	0.1706	0.476
B97-D /6-31G(d)	0.0209	0.0494	0.0701	0.1727	0.4858
B97-D /6-31G(p)	0.0209	0.0386	0.069	0.1556	0.476
B97-D /6-31G(d,p)	0.021	0.0392	0.0697	0.1567	0.4858
B97-D /6-31G(2d,p)	0.0205	0.0386	0.0688	0.1558	0.4847
B97-D /6-311G	0.021	0.0401	0.0684	0.1581	0.4781
B97-D /6-311G(d)	0.0207	0.0391	0.068	0.1584	0.4803
B97-D /6-311G(p)	0.0213	0.0387	0.0683	0.1543	0.4761
B97-D /6-311G(d,p)	0.0211	0.0388	0.068	0.1536	0.4817
B97-D /6-311G(2d,p)	0.0214	0.0393	0.0695	0.1556	0.483
B97-D /6-311G(2df,2pd)	0.0213	0.0389	0.0682	0.1531	0.4799
B97-D /TZV(p)	0.0226	0.0408	0.0708	0.1592	0.4931
B97-D /TZV(2p)	0.0228	0.0411	0.0713	0.1603	0.4931
B97-D /Def2-TZVP	0.0217	0.0395	0.0684	0.1543	0.4783
B97-D /Def2-TZVPP	0.0218	0.0397	0.0684	0.1543	0.4782
B97-D /6-31+G(d,p)	0.0318	DNC	0.1565	0.1933	0.484
B97-D /6-31+G(2d,p)	0.0526	0.0644	0.1439	0.2179	0.5156
B97-D /6-311+G	DNC	DNC	0.4455	0.349	0.5354
B97-D /6-311+G(d,p)	DNC	DNC	0.1841	0.298	0.6294
B97-D /6-311+G(2d,p)	0.0347	DNC	DNC	0.2454	0.6529

DNC= data not converged

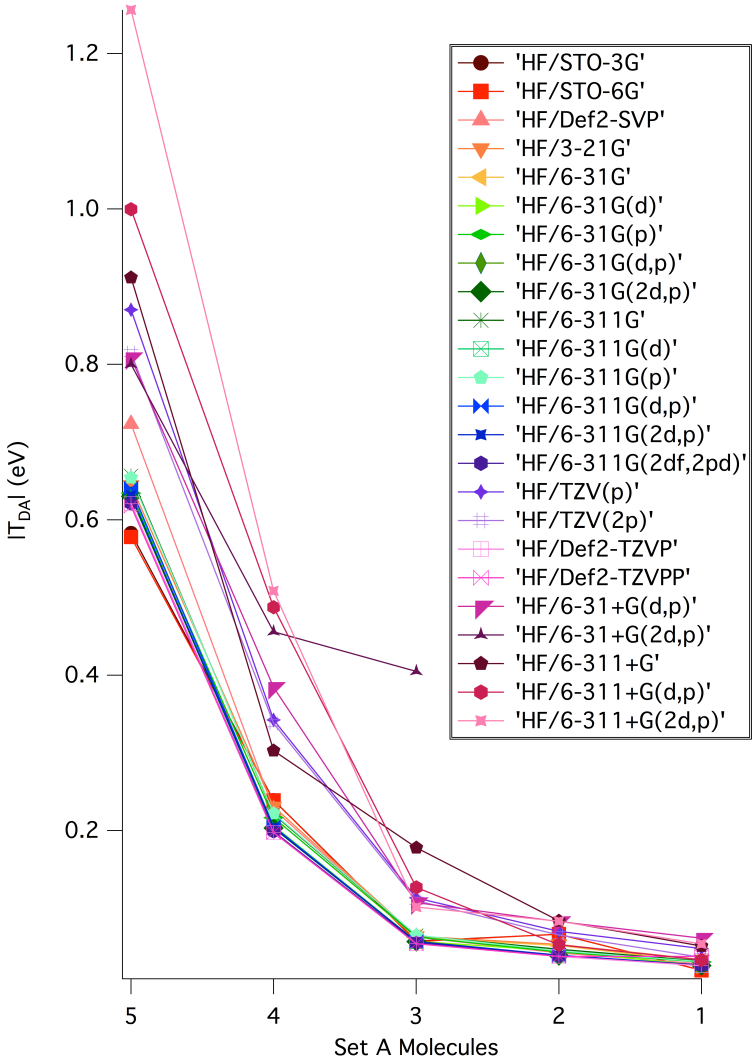

Figure S1. Analogous basis set study conducted with Hartree-Fock for T_{DA} predictions of Set A molecules 1-5, yielding the same overestimation of T_{DA} when pairing to diffuse basis sets.

Table S2. Raw data from Figure S1, for Hartree-Fock basis set study, T_{DA} predictions in (eV) for Set A molecules 1-5.

	$\|T_{DA}\|$ (eV)				
	Molecule				
Method/Basis:	**1**	**2**	**3**	**4**	**5**
HF/STO-3G	0.5828	0.2392	0.0579	0.0667	0.0204
HF/STO-6G	0.5778	0.2390	0.0571	0.0670	0.0202
HF/Def2-SVP	0.7233	0.2275	0.0631	0.0428	0.0284
HF/3-21G	0.6447	0.2310	0.0641	0.0536	0.0339
HF/6-31G	0.6308	0.2169	0.0622	0.0522	0.0310
HF/6-31G(d)	0.6281	0.2066	0.0577	0.0450	0.0264
HF/6-31G(p)	0.6343	0.2166	0.0577	0.0440	0.0309
HF/6-31G(d,p)	0.6287	0.2034	0.0576	0.0394	0.0267
HF/6-31G(2d,p)	0.6302	0.2032	0.0572	0.0391	0.0263
HF/6-311G	0.6565	0.2210	0.0651	0.0473	0.0322
HF/6-311G(d)	0.6381	0.2059	0.0572	0.0398	0.0266
HF/6-311G(p)	0.6542	0.2221	0.0655	0.0453	0.0314
HF/6-311G(d,p)	0.6405	0.2052	0.0572	0.0397	0.0270

HF/6-311G(2d,p)	0.6312	0.2039	0.0572	0.0393	0.0270
HF/6-311G(2df,2pd)	0.6207	0.1990	0.0556	0.0385	0.0266
HF/TZV(p)	0.8702	0.3424	0.1132	0.0703	0.0481
HF/TZV(2p)	0.8148	0.3382	0.1099	0.0656	0.0371
HF/Def2-TZVP	0.6209	0.1975	0.0545	0.0381	0.0262
HF/Def2-TZVPP	0.6173	0.1975	0.0545	0.0381	0.0381
HF/6-31+G(d,p)	0.8086	0.3843	0.1073	0.0829	0.0616
HF/6-31+G(2d,p)	0.8001	0.4560	0.4049	DNC	DNC
HF/6-311+G	0.9116	0.3029	0.2202	0.0838	0.0515
HF/6-311+G(d,p)	0.9996	0.4875	0.1269	0.0532	0.0336
HF/6-311+G(2d,p)	1.2561	0.5085	0.1016	0.0833	0.0543

DNC= data not converged

Table S3. Full tabulation of calculated T_{DA} (eV) coupling elements for Set B as a function of density functional type and orbital localization method, using the 6-311G(2df,2pd) basis set. MAE error presented with respect to experimental measurements of T_{DA} (photoelectron spectroscopy exeriments[40] determining IP_1 and IP_2, such that T_{DA} is ½ΔIP

		Pipek-Mezey Localization applied to T_{DA} (eV) predictions										
Molecule	**Expt.[40] T_{DA} (eV)**	**B3LYP**	**BLYP**	**PBE**	**PBE0**	**M06-L**	**M06**	**M06-2X**	**M06-HF**	**B97-D**	**wB97X-D**	**RHF**
4	**0.16**	0.164	0.148	0.159	0.181	0.160	0.164	0.206	0.281	0.153	0.195	0.199
5	**0.435**	0.509	0.473	0.491	0.542	0.494	0.515	0.580	0.687	0.480	0.566	0.621
6	**0.43**	0.496	0.473	0.445	0.484	0.447	0.469	0.472	0.517	0.460	0.490	0.652
7	**0.22**	0.195	0.175	0.180	0.209	0.192	0.198	0.244	0.317	0.180	0.226	0.252
8	**0.63**	0.798	0.737	0.762	0.837	0.790	0.794	0.869	1.037	0.751	0.881	1.026
9	**0.215**	0.262	0.242	0.253	0.282	0.252	0.262	0.294	0.366	0.246	0.295	0.322
10	**0.26**	0.343	0.326	0.351	0.371	0.341	0.344	0.393	0.462	0.332	0.395	0.374
11	**0.09**	0.097	0.094	0.101	0.104	0.090	0.095	0.116	0.146	0.096	0.109	0.092
	MAE Error:	**0.059**	**0.028**	**0.048**	**0.074**	**0.048**	**0.050**	**0.092**	**0.172**	**0.044**	**0.089**	**0.137**
		Boys Localization applied to T_{DA} (eV) predictions										
Molecule	**Expt.[40] T_{DA} (eV)**	**B3LYP**	**BLYP**	**PBE**	**PBE0**	**M06-L**	**M06**	**M06-2X**	**M06-HF**	**B97-D**	**wB97-D**	**RHF**
4	**0.16**	0.322	0.290	0.310	0.352	0.313	0.324	0.384	0.530	0.301	0.377	0.390
5	**0.435**	0.986	0.913	0.951	1.051	0.966	0.995	1.124	1.332	0.930	1.099	1.184
6	**0.43**	0.939	0.873	0.861	0.946	0.870	0.908	0.922	0.993	0.876	0.950	1.249
7	**0.22**	0.378	0.341	0.349	0.408	0.374	0.384	0.475	0.619	0.351	0.436	0.479
8	**0.63**	1.561	1.429	1.410	1.615	1.406	1.502	1.678	1.993	1.400	1.660	2.082
9	**0.215**	0.511	0.469	0.789	0.550	0.492	0.511	0.577	0.705	0.480	0.578	0.612
10	**0.26**	0.658	0.629	0.681	0.714	0.652	0.659	0.760	0.884	0.638	0.753	0.698
11	**0.09**	0.187	0.183	0.190	0.202	0.180	0.184	0.232	0.287	0.181	0.209	0.171
	MAE error:	**0.388**	**0.336**	**0.388**	**0.425**	**0.352**	**0.378**	**0.464**	**0.613**	**0.340**	**0.453**	**0.553**
		E-R Localization applied to T_{DA} (eV) predictions										
Molecule	**Expt.[40] T_{DA} (eV)**	**B3LYP**	**BLYP**	**PBE**	**PBE0**	**M06-L**	**M06**	**M06-2X**	**M06-HF**	**B97-D**	**wB97-D**	**RHF**

4	**0.16**	0.305	0.275	0.298	0.357	0.550	0.309	0.389	0.550	0.305	0.364	0.366
5	**0.435**	0.951	0.881	0.929	1.019	1.294	0.958	1.097	1.293	0.900	1.066	1.152
6	**0.43**	0.915	0.852	0.846	0.926	0.972	0.890	0.905	0.972	0.858	0.932	1.219
7	**0.22**	0.364	0.326	0.342	0.394	0.598	0.370	0.465	0.598	0.180	0.424	0.465
8	**0.63**	1.388	1.285	1.336	1.464	1.836	1.385	1.560	1.836	1.295	1.537	1.754
9	**0.215**	0.484	0.445	0.476	0.526	0.678	0.488	0.553	0.678	0.458	0.551	0.592
10	**0.26**	0.626	0.637	0.683	0.684	0.909	0.629	0.730	0.909	0.644	0.769	0.671
11	**0.09**	0.178	0.173	0.188	0.194	0.280	0.176	0.223	0.280	0.177	0.203	0.166
	MAE Error:	**0.347**	**0.304**	**0.332**	**0.391**	**0.585**	**0.346**	**0.435**	**0.585**	**0.307**	**0.426**	**0.493**

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