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Electric Supporting Information (ESI) for:

Structure and Reactivity/Selectivity Control by Oriented Electric Fields

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I. Methodology for Calculations of OEEF Effects on Bonds

The text of this tutorial contains, in addition to reactivity, also discussions of oriented-external electric field (OEEF) effects on various bonds. By and large, three computational procedures were used in the presence of OEEF. One involves density functional theoretic (DFT) calculations, and the second, ab-initio valence bond (VB) calculations. For the cases of H in OEEF, and the rotational barrier of $H_2C{=}CH_2$, we used CASSCF.

DFT Calculation: The B3LYP functional was used with the following basis sets (B): cc-pVTZ, for I_2 we used cc-pVTZ-PP and cc-pVTZ-DK with DKH2 correction, and in the presence of OEEF, hence B3LYP/B/OEEF. These calculations were used for geometry optimization as well as for finding the critical OEEF along the bond axis Z, which is required to dissociate the bond, $F_{Z(\mathrm{dis})}$. In all cases studied, the bonds dissociated into ions. Some examples are given in Tables S1-S9. All calculations used GAUSSIAN 09.[S1] Note that in most of the tables below, we specify the atoms, which are placed in the negative- and positive-directions along the Z axis, using Z<0 or Z>0 notation, respectively and also specify the sign of the OEEF using F_Z in the GAUSSIAN convention (see scheme S1).

Scheme S1. F_z convention and explanation for Z axis notation used in the tutorial.

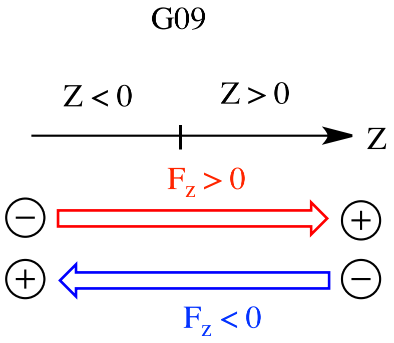

Table S1. Dependence, of the equilibrium bond length (R, Å), total energy (E, au) and Mulliken charges of the atoms, on the strength of applied electric field (F_Z, au) for H_2 using B3LYP/cc-pVTZ level of theory. The bond length was re-optimized at each F_Z value.

			Mulliken charges	
F_Z	R	E	H[a]	H[b]
0.0	0.7428	-1.1799988	0.000	0.000
0.01	0.7439	-1.1803419	0.059	-0.059
0.1	0.8062	-1.2164293	0.592	-0.592
0.11	0.8255	-1.2247346	0.654	-0.654
0.12	0.8503	-1.2341829	0.717	-0.717
0.13	0.8871	-1.2449804	0.784	-0.784
0.14	0.9556	-1.2575720	0.861	-0.861
0.15	dissoc.[c]			

[a]The first charge corresponds to the H atom (in H-H), which is placed in the Z<0 direction. [b]The second charge corresponds to the H atom, which is placed at the Z>0 direction. [c]At this F_Z the molecule dissociates to ions.

Table S2. Dependence, of the equilibrium bond length (R, Å), total energy (E, au) and Mulliken charges of the atoms, on the strength of applied electric field (F_Z, au) for Li_2 using B3LYP/cc-pVTZ level of theory. The bond length was re-optimized at each F_Z value.

			Mulliken charges	
F_Z	R	E	Li[a]	Li[b]
0.0	2.6933	-0.0172062	0.000	0.000
0.01	2.8625	-0.0311803	-0.246	0.246
0.015	3.5150	-0.0532564	-0.237	0.237
0.017	dissoc.[c,d]			

[a]The first charge corresponds to the Li atom (in Li-Li), which is placed in the Z<0 direction. [b]The second charge corresponds to the Li atom, which is placed at the Z>0 direction. [c]At this F_Z the molecule dissociates to ions. [d]Note that the Na_2 molecule dissociated to ions already at $F_Z = 0.015$ au.

Table S3. Dependence, of the equilibrium bond length (R, Å), total energy (E, -199.0 au) and Mulliken charges of the atoms, on the strength of applied electric field (F_Z, au) for F_2; using B3LYP/cc-pVTZ level of theory. The bond length was re-optimized at each F_Z value.

			Mulliken charges	
F_Z	R	E	F[a]	F[b]
0.0	1.3873	-0.5863963	0.000	0.000
0.01	1.3978	-0.5869249	0.033	-0.033
0.10	1.4746	-0.6420571	0.355	-0.355
0.11	1.4981	-0.6546340	0.399	-0.399
0.12	1.5284	-0.6688999	0.448	-0.448
0.13	1.5747	-0.6851645	0.504	-0.504
0.14	1.6939	-0.7042421	0.591	-0.591
0.15	dissoc[c]			

[a]The first charge corresponds to the F atom placed in the Z<0 direction. [b]The second charge corresponds to the F atom placed at the Z>0 direction. [c]At this F_Z the molecule dissociates to ions.

Table S4. Dependence, of the equilibrium bond length (R, Å), total energy (E, -920.0 au) and Mulliken charges of the atoms, on the strength of applied electric field (F_Z, au) for Cl_2; using B3LYP/cc-pVTZ level of theory. The bond length was re-optimized at each F_Z value.

			Mulliken charges	
F_Z	R	E	Cl[a]	Cl[b]
0.0	2.0234	-0.4352474	0.000	0.000
0.01	2.0256	-0.4371105	0.070	-0.070
0.02	2.0330	-0.4427242	0.141	-0.141
0.03	2.0462	-0.4521662	0.213	-0.213
0.04	2.0668	-0.4655822	0.290	-0.290
0.05	2.0985	-0.4832209	0.372	-0.372
0.06	2.1496	-0.5055287	0.464	-0.464
0.07	2.2563	-0.5335209	0.581	-0.581
0.08	dissoc[c]			

[a]The first charge corresponds to the Cl placed in the Z<0 direction. [b]The second charge corresponds to the Cl placed at the Z>0 direction. [c]At this F_Z the molecule dissociates to ions.

Table S5. Dependence, of the equilibrium bond length (R, Å), total energy (E, -591.0 au) and Mulliken charges of the atoms, on the strength of applied electric field (F_Z, au) for I_2; using B3LYP/cc-pVTZ level of theory. The bond length was re-optimized at each F_Z value.

			Mulliken charges	
F_Z	R	E	I[a]	I[b]
0.0	2.7030	-0.6928111	0.000	0.000
0.0[c]	2.6910	-0.4128544	0.000	0.000
0.01	2.7100	-0.6973375	0.130	-0.130
0.01[c]	2.7038[c]	-0.4173923	0.128	-0.128
0.02	2.7329	-0.7110333	0.262	-0.262
0.03	2.7795	-0.7343061	0.398	-0.398
0.04	2.8757	-0.7681443	0.544	-0.544
0.05	dissoc[d]			

[a]The first charge corresponds to the I placed in the Z<0 direction. [b]The second charge corresponds to the I placed at the Z>0 direction [c]Result for all electrons relativistic B3LYP/cc-pVTZ-DK level (-14227.0 au) with DKH2. [d]At this F_Z the molecule dissociates to ions.

Table S6. Dependence, of the equilibrium bond length (R, Å), total energy (E, -460.0 au) and Mulliken charges of the atoms, on the strength of applied electric field (F_Z, au) for HCl; calculated with B3LYP/cc-pVTZ level of theory. The bond length was re-optimized at each F_Z value.

F_Z	R	E	H[a]	Cl[b]
0.0	1.2836	-0.8430388	0.159	-0.159
0.01	1.2871	-0.8485510	0.202	-0.202
0.05	1.3213	-0.8859545	0.365	-0.365
0.10	1.4738	-0.9711954	0.617	-0.617

0.11	dissoc[c]			
-0.01	1.2812	-0.8390633	0.115	-0.115
-0.05	1.2900	-0.8392461	-0.090	0.090
-0.10	1.3759	-0.8832440	-0.459	0.459
-0.11	1.4260	-0.9002835	-0.560	0.560
-0.12	dissoc[c]			

[a]The first charge corresponds to the H at (in H-Cl), which is placed in the Z<0 direction. [b]The second charge corresponds to the Cl atm, placed in the Z>0 direction. [c]At this F_Z the molecule dissociates to ions.

Table S7. Dependence, of the equilibrium bond length (R, Å), total energy (E, -500.0 au) and Mulliken charges of the atoms, on the strength of applied electric field (F_Z, au) for H_3C-Cl; calculated with B3LYP/cc-pVTZ level of theory. The bond length was re-optimized at each F_Z value.

			Mulliken charges		
F_Z	R	E	C[a]	H_3C[b]	Cl[c]
0.0	1.8002	-0.1644777	-0.201	0.169	-0.169
0.01	1.8187	-0.1739794	-0.175	0.246	-0.246
0.02	1.8450	-0.1870617	-0.143	0.327	-0.327
0.03	1.8841	-0.2039740	-0.102	0.416	-0.416
0.04	1.9521	-0.2252617	-0.040	0.523	-0.523
0.05	2.2025	-0.2527999	0.102	0.717	-0.717
0.06	dissoc[d]				
-0.01	1.7872	-0.1584413	-0.222	0.094	-0.094
-0.02	1.7775	-0.1558398	-0.239	0.018	-0.018
-0.04	1.7649	-0.1611601	-0.258	-0.141	0.141
-0.06	1.7584	-0.1816334	-0.246	-0.322	0.322
-0.07	1.7537	-0.1984008	-0.213	-0.428	0.428
-0.08	1.7473	-0.2203680	-0.148	-0.551	0.551
-0.09	1.7388	-0.2485539	-0.041	-0.694	0.694
-0.10	1.7326	-0.2842507	0.099	-0.835	0.835
-0.11	dissoc[d]				

[a]The first charge corresponds to the C atom (in H_3C-Cl), which is placed in the Z<0 direction. [b] Charge on the H_3C group placed in the Z<0 direction. [c]Charge corresponds to the Cl placed in the Z>0 direction. [d]At this F_Z the molecule dissociates to ions.

Table S8. Dependence, of the equilibrium bond length (R, Å), total energy (E, -618.0 au) and Mulliken charges of the atoms, on the strength of applied electric field (F_Z, au) for Me_3C-Cl; calculated with B3LYP/cc-pVTZ level of theory. The bond length was re-optimized at each F_Z value.

			Mulliken charges		
F_Z	R	E	C[a]	Me_3C[b]	Cl[c]
0.0	1.8595	-0.1574552	0.103	0.220	-0.220
0.01	1.9061	-0.1705213	0.116	0.332	-0.332
0.02	2.0053	-0.1920442	0.135	0.476	-0.476

0.025	2.2285	-0.2071985	0.155	0.638	-0.638
0.03	dissoc[d]				
-0.01	1.8324	-0.1519888	0.091	0.120	-0.120
-0.02	1.8151	-0.1539516	0.079	0.024	-0.024
-0.03	1.8042	-0.1635044	0.065	-0.073	0.073
-0.04	1.7987	-0.1811075	0.049	-0.173	0.173
-0.05	1.7993	-0.2076251	0.028	-0.283	0.283
-0.06	1.8083	-0.2445527	0.004	-0.411	0.411
-0.07	1.8257	-0.2942568	-0.022	-0.563	0.563
-0.08	1.8707	-0.3598273	-0.046	-0.739	0.739
-0.09	2.004	-0.4450903	-0.063	-0.939	0.939
-0.10	dissoc[d]				

[a] The first charge corresponds to the C atom (in Me_3C-Cl), which is placed in the Z<0 direction. [b] Charge on the Me_3C group. [c] Charge corresponds to the Cl atom, which is placed in the Z>0 direction. [d] At this F_Z the molecule dissociates to ions.

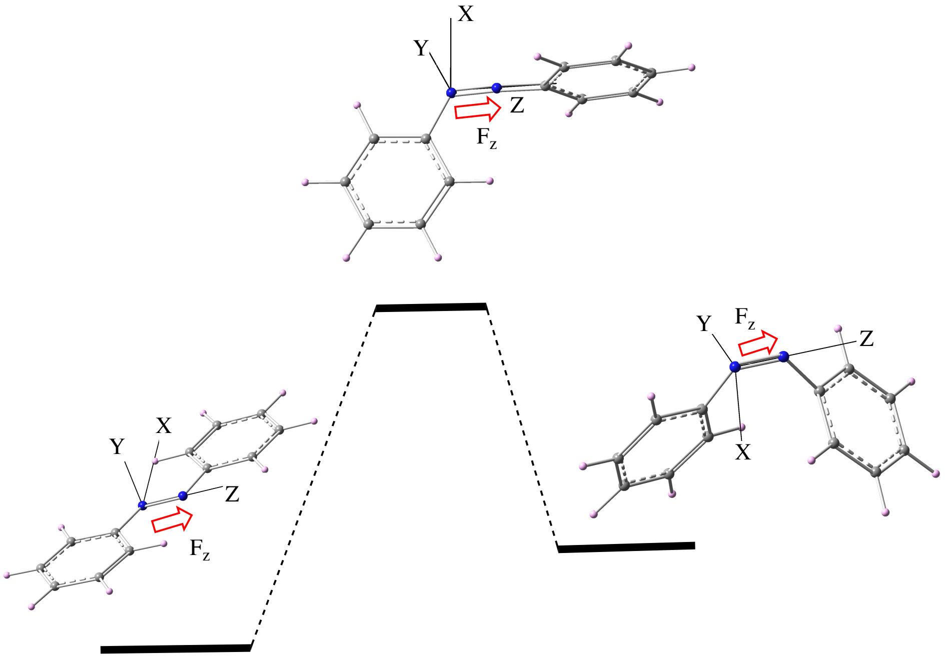

Figure S1. Trans-cis isomerization of azobenzene via the N-inversion mechanism

Table S9. Total energies of azobenzene (E_t, au) for trans, cis and TS (Fig. S1), imaginary frequencies of TS (iFreq, cm^{-1}), isomerization barrier ($\Delta E^{\#}$, kcal mol^{-1}) and trans →cis energy difference ($\Delta E_{t\text{-}c}$, kcal mol^{-1}) calculated by B3LYP/cc-pVTZ.

	E_t(trans)	E_t(cis)	E_t(TS)	iFreq	$\Delta E^{\ddagger}$	$\Delta E_{t\text{-}c}$
F_Z=0.0	-572.959636	-572.935234	-572.897150	-419.66	39.21 (23.9)[a]	15.31
F_Z=0.0125	-572.977313	-572.954061	-572.931483	-293.91	28.76 (14.2)[a]	19.24

F_Z=0.0175	-572.994994	-572.973962	-572.954061	-242.50	21.81 (12.4)[a]	13.20
F_Z=0.0225	-573.019669	-573.003629	-572.999564	-151.13	12.62 (2.6)[a]	10.06
F_Z=0.0125 F_Y=0.0125	-572.987900	-572.968839	-572.941741	-377.33	28.97 (17.0)[a]	11.96
F_Z=0.0125 F_Z=0.0125	-573.012319	-572.952163	-572.923494	-306.29	55.74 (18.0)[a]	37.75
F_Z=-0.0125	-572.977312	-572.954053	-572.915985	-481.40	38.48 (23.9)[a]	14.60

[a] Barrier from cis to trans.

VB Calculations: Generally, VBSCF was used with a few basis sets, B, and in the absence/presence of OEEF along the bond axis, hence VBSCF/B/OEEF. Typically, B = 6-311+G**. The breathing-orbital VB (BOVB) method,[S2] was used to test some of the VBSCF results. All VB calculations used the XMVB package.[S3] examples are given in Tables S10 – S25.

Table S10. F_Z dependence of total energies (E, F_Z in au), weights of the covalent and ionic structures and VB Mulliken charges of the atoms for H_2; calculated with VBSCF/6-311G(p). At each F_Z value the B3LYP/cc-pVTZ optimized geometry was used.

		Weights of the VB structures			VB charges	
F_Z	E (au)	$H\cdot\ \cdot H$	$H^{-}\ {}^{+}H^{a}$	$H^{+}\ {}^{-}H^{b}$	H^{c}	H^{d}
0.0	-1.150386	0.821	0.089	0.089	0.000	0.000
-0.1	-1.180367	0.530	0.470	0.000	-0.491	0.491
-0.1^{e}	-1.182792^{e}	0.466^{e}	0.532^{e}	0.001^{e}	-0.531^{e}	0.531^{e}
-0.11	-1.187214	0.467	0.543	0.000	-0.551	0.551
-0.11^{e}	-1.189915^{e}	0.412^{e}	0.568^{e}	0.000^{e}	-0.587^{e}	0.587^{e}
-0.12	-1.195026	0.398	0.602	0.000	-0.616	0.616
-0.12^{e}	-1.197981^{e}	0.354^{e}	0.646^{e}	0.000^{e}	-0.646^{e}	0.646^{e}

[a] Weight of the ionic structure where negative charge on the H atom placed in the Z<0 direction.
[b] Weight of the ionic structure where negative charge on the H atom placed in the Z>0 direction.
[c] Charge corresponds to the H atom (in H-H), which is placed in the Z<0 direction. [d] Charge corresponds to the H atom (in H-H) placed in the Z>0 direction. [e] Results at the BOVB/6-311G(p) level.

Table S11. F_Z (au) dependence of total energies (E, -14.0 au), weights of the covalent and ionic structures and VB Mulliken charges of the atoms for Li_2; calculated with VBSCF/6-311G(p). At each F_Z value the B3LYP/cc-pVTZ optimized geometry was used.

		Weights of the VB structures			VB charges	
F_Z	E (au)	$Li\cdot\ \cdot Li$	$Li^{-}\ {}^{+}Li^{a}$	$Li^{+}\ {}^{-}Li^{b}$	Li^{c}	Li^{d}

0.0	-0.877797	0.998	0.001	0.001	0.000	0.000
-0.01	-0.898088	0.913	0.079	0.008	-0.089	0.089
-0.015	-0.917390	0.882	0.107	0.011	-0.096	0.096

[a] Weight of the ionic structure where negative charge on the Li atom placed in the Z<0 direction. [b] Weight of the ionic structure where negative charge on the Li atom placed in the Z>0 direction. [c] Charge corresponds to the Li atom (in Li-Li), which is placed in the Z<0 direction. [d] Charge corresponds to the Li atom placed in the Z>0 direction.

Table S12. F_Z (au) dependence of total energies (E, -198.0 au), weights of the covalent and ionic structures and VB Mulliken charges of the atoms on the strength of applied electric field (F_z, au) for F_2; calculated with VBSCF/6-311G(d). At each F_Z value the B3LYP/cc-pVTZ optimized geometry was used.

		Weights of the VB structures			VB charges	
F_Z	E	$F\cdot\ \cdot F$	$F^-\ {}^+F$[a]	$F^+\ {}^-F$[b]	F[c]	F[d]
0.0	-0.790868	0.772	0.114	0.114	0.000	0.000
-0.1	-0.839491	0.712	0.260	0.028	-0.240	0.240
-0.11	-0.849658	0.693	0.286	0.021	-0.274	0.274
-0.12	-0.861090	0.665	0.321	0.014	-0.315	0.315
-0.13	-0.874017	0.621	0.372	0.007	-0.372	0.372
-0.13	-0.915123[e]	0.550[e]	0.4365[e]	0.015[e]	-0.429[e]	0.429[e]
-0.14	-0.888394	0.498	0.502	0.000	-0.507	0.507
-0.14	-0.931017[e]	0.488[e]	0.506[e]	0.006[e]	-0.506[e]	0.506[e]
-0.15[f]	-0.912158	0.273	0.727	0.000	-0.732	0.732

[a] Weight of the ionic structure where negative charge on the F atom placed in the Z<0 direction. [b] Weight of the ionic structure where negative charge on the F atom placed in the Z>0 direction. [c] Charge corresponds to the F atom placed in the Z<0 direction. [d] Charge corresponds to the F atom placed in the Z>0 direction. [e] BOVB/6-311G(d) results. [f] Result for F_Z=-0.15 au was calculated at the F-F distance equal 1.8Å.

Table S13. F_Z (au) dependence of total energies (E, -918.0 au), weights of the covalent and ionic structures and VB Mulliken charges of the atoms for Cl_2; calculated with VBSCF/6-311G(d) level of theory. At each F_Z value the B3LYP/cc-pVTZ optimized geometry was used.

		Weights of the VB structures			VB charges	
F_Z	E	$Cl\cdot\ \cdot Cl$	$Cl^-\ {}^+Cl$[a]	$Cl^+\ {}^-Cl$[b]	Cl[c]	Cl[d]
0.0	-0.979228	0.692	0.154	0.154	0.000	0.000
-0.04	-1.006820	0.627	0.320	0.054	-0.266	0.266
-0.05	-1.023460	0.582	0.383	0.035	-0.348	0.348
-0.05	-1.038871[e]	0.553[e]	0.404[e]	0.043[e]	-0.360[e]	0.360[e]
-0.06	-1.045366	0.515	0.466	0.019	-0.446	0.447
-0.06	-1.061172[e]	0.498[e]	0.477[e]	0.025[e]	-0.451[e]	0.451[e]
-0.07	-1.075487	0.395	0.599	0.005	-0.595	0.595
-0.07	-1.091316[e]	0.407[e]	0.583[e]	0.009[e]	-0.574[e]	0.574[e]

[a] Weight of the ionic structure where negative charge on the Cl atom placed in the Z<0 direction. [b] Weight of the ionic structure where negative charge on the Cl atom placed in the Z>0 direction.

[c]Charge corresponds to the Cl atom placed in the Z<0 direction. [d]Charge corresponds to the Cl atom placed in the Z>0 direction. [e]BOVB/6-311G(d) results.

Table S14. F_Z (au) dependence of total energies (E, -589.0 au), weights of the covalent and ionic structures and VB Mulliken charges of the atoms for I_2; calculated with VBSCF/cc-pVTZ-PP. At each F_Z value the B3LYP/cc-pVTZ optimized geometry was used.

		Weights of the VB structures			VB charges	
F_Z	E	$\mathrm{I\cdot\ \cdot I}$	$\mathrm{I^{-}\ {}^{+}I}$[a]	$\mathrm{I^{+}\ {}^{-}I}$[b]	I[c]	I[d]
0.0	-0.358069	0.708	0.146	0.146	0.000	0.000
-0.01	-0.362481	0.701	0.190	0.109	0.093	-0.093
-0.02	-0.375849	0.681	0.242	0.077	0.188	-0.188
-0.03	-0.398653	0.639	0.314	0.047	0.297	-0.297
-0.04	-0.432162	0.554	0.427	0.019	0.441	-0.441
-0.05[e]	-0.479740	0.385	0.613	0.002	0.642	-0.642

[a]Weight of the ionic structure where negative charge on the I atom placed in the Z<0 direction. [b]Weight of the ionic structure where negative charge on the I atom placed in the Z>0 direction. [c]Charge corresponds to the I atom placed in the Z<0 direction. [d]Charge corresponds to the I atom placed in the Z>0 direction. [e]For F_Z=-0.05 au at the I-I distance of 3.0Å.

Table S15. F_Z (au) dependence of total energies (E, -460.0 au), weights of the covalent and ionic structures and VB Mulliken charges of the atoms for HCl; calculated with VBSCF/6-311G(d,p). At each F_Z value the B3LYP/cc-pVTZ optimized geometry was used.

		Weights of the VB structures			VB charges	
F_Z	E	$\mathrm{H\cdot\ \cdot Cl}$	$\mathrm{H^{-}\ {}^{+}Cl}$[a]	$\mathrm{H^{+}\ {}^{-}Cl}$[b]	H[c]	Cl[d]
0.0	-0.108224	0.697	0.074	0.229	0.154	-0.154
-0.01	-0.102428	0.703	0.091	0.205	0.114	-0.114
-0.05	-0.091529	0.695	0.181	0.124	-0.057	0.057
-0.10	-0.114327	0.557	0.401	0.042	-0.360	0.360
-0.11	-0.127400	0.486	0.487	0.027	-0.460	0.460
-0.12	-0.141629	0.419	0.562	0.019	-0.543	0.543
-0.12	dissoc[f]					
0.01	-0.115158	0.687	0.060	0.253	0.194	-0.194
0.05	-0.154214	0.617	0.016	0.368	0.352	-0.352
0.10	-0.230944	0.412	0.000	0.597	0.607	-0.607
0.11	-0.251498	0.373	0.000	0.637	0.646	-0.646
0.11	dissoc[f]					

[a]Weight of the ionic structure where negative charge on the H atom placed in the Z<0 direction. [b]Weight of the ionic structure where negative charge on the Cl atom placed in the Z>0 direction. [c]Charge corresponds to the H atom placed in the Z<0 direction. [d]Charge corresponds to the Cl atom placed in the Z>0 direction. [f]At this F_Z the molecule dissociates to the ions.

Table S16. Bond dissociation energy (D_e, kcal mol^{-1}) and RE_{CS} (kcal mol^{-1}) of HCl molecule calculated at different F_Z values (au). Total energies (E_t, au) at the optimal distance, 1.3 Å, and the long distance at 7.0Å.

F_Z	D_e	RE_{CS}	E_t at 1.3Å	E_t at 7.0Å	D_e[a]	D_e[b]
0.0	84.86	19.57	-460.108414	-459.973181	103.63	91.29
+0.02	93.45	33.46	-460.123318	-459.974387	112.35	99.08
-0.02	77.63	2.35	-460.098091	-459.974383	98.33	85.02

[a] D_e from B3LYP/6-311G(d,p) calculations. [b] D_e from BOVB/6-311G(d,p) calculations.

Table S17. Total energies (E_t, au), energy of covalent structure (E_{cov}, au), energy of $H^{+}\ {}^{-}Cl$ ionic structure (E_{ion}, au) at optimal distance of 1.3Å and energy difference between covalent and ionic structures at 1.3Å and bond dissociation energy (D_e, kcal mol^{-1}).

F_Z	E_t	E_{cov}	E_{ion}	$\Delta E_{cov\text{-}ion}$	D_e
0.0	-460.108414	-460.077229	-459.896799	0.18043	84.86
+0.02	-460.123318	-460.070000	-459.934307	0.13569	93.45
-0.02	-460.098091	-460.087168	-459.861247	0.22592	77.63

Table S18. Dependence of total energies (E, -459.0 au), weights of the covalent and ionic structures, and VB Mulliken charges of the atoms, on the H-Cl bond length (Å) for HCl; calculated with VBSCF/6-311G(d,p) level of theory at F_Z=+0.02 au.

		Weights of the VB structures			VB charges	
R	E	H· ·Cl	$H^{-}\ {}^{+}Cl$[a]	$H^{+}\ {}^{-}Cl$[b]	H[c]	Cl[d]
1.10	-1.089687	0.692	0.059	0.248	0.189	-0.189
1.15	-1.105828	0.686	0.057	0.257	0.200	-0.200
1.20	-1.115943	0.681	0.054	0.266	0.212	-0.212
1.25	-1.121414	0.677	0.050	0.273	0.224	-0.224
1.30	**-1.123318**	0.674	0.046	0.280	0.234	-0.234
1.35	-1.122495	0.672	0.042	0.286	0.244	-0.244
1.40	-1.119610	0.671	0.038	0.291	0.253	-0.253
1.45	-1.115179	0.671	0.034	0.295	0.261	-0.261
1.50	-1.109620	0.672	0.031	0.297	0.267	-0.267
1.75	-1.074283	0.695	0.016	0.289	0.273	-0.273
2.00	-1.039631	0.746	0.007	0.247	0.240	-0.240
2.50	-0.995350	0.889	0.001	0.111	0.110	-0.110
3.00	-0.979558	0.970	0.000	0.030	0.030	-0.030
6.00	-0.974389	1.000	0.000	0.000	0.000	-0.000
7.00	-0.974387	1.000	0.000	0.000	0.000	0.000

[a] Weight of the ionic structure where negative charge on the H atom placed in the Z<0 direction. [b] Weight of the ionic structure where negative charge on the Cl atom placed in the Z>0 direction. [c] Charge corresponds to the H atom placed in the Z<0 direction. [d] Charge corresponds to the Cl atom placed in the Z>0 direction.

Table S19. Dependence of total energies (E, -459.0 au), weights of the covalent and ionic structures, and VB Mulliken charges of the atoms, on the H-Cl bond length (Å) HCl; calculated with VBSCF/6-311G(d,p) level of theory at F_Z= -0.02 au.

		Weights of the VB structures			VB charges	
R	E	H· ·Cl	$H^{-}\ {}^{+}Cl$[a]	$H^{+}\ {}^{-}Cl$[b]	H[c]	Cl[d]

1.10	-1.065784	0.708	0.116	0.175	0.059	-0.059
1.15	-1.081520	0.706	0.115	0.180	0.065	-0.065
1.20	-1.091278	0.705	0.113	0.182	0.069	-0.069
1.25	-1.096440	0.705	0.111	0.184	0.073	-0.073
1.30	**-1.098091**	0.708	0.109	0.184	0.075	-0.075
1.35	-1.097078	0.712	0.106	0.182	0.077	-0.077
1.40	-1.094068	0.717	0.103	0.180	0.077	-0.077
1.45	-1.089591	0.724	0.099	0.177	0.077	-0.077
1.50	-1.084067	0.732	0.096	0.172	0.076	-0.076
1.75	-1.050387	0.789	0.076	0.135	0.059	-0.059
2.00	-1.020037	0.859	0.054	0.087	0.033	-0.033
2.50	-0.986970	0.960	0.019	0.022	0.003	-0.003
3.00	-0.977207	0.991	0.005	0.004	0.001	-0.001
6.00	-0.974382	1.000	0.000	0.000	0.000	-0.000
7.00	-0.974383	1.000	0.000	0.000	0.000	0.000

[a]Weight of the ionic structure where negative charge on the H atom placed in the Z<0 direction. [b]Weight of the ionic structure where negative charge on the Cl atom placed in the Z>0 direction. [c]Charge corresponds to the H atom placed in the Z<0 direction. [d]Charge corresponds to the Cl atom placed in the Z>0 direction.

Table S20. Dependence of total energies (E, -459.0 au), weights of the covalent and ionic structures, and VB Mulliken charges of the atoms, on the H-Cl bond length (Å); calculated with VBSCF/6-311G(d,p) level of theory at F_Z=-0.12 au.

		Weights of the VB structures			VB charges	
R	E	H· ·Cl	H$^-$ $^+$Cl[a]	H$^+$ $^-$Cl[b]	H[c]	Cl[d]
1.10	-1.071709	0.532	0.416	0.052	-0.364	0.364
1.15	-1.092595	0.520	0.432	0.048	-0.384	0.384
1.20	-1.108145	0.506	0.451	0.043	-0.408	0.408
1.25	-1.119707	0.491	0.471	0.038	-0.434	0.434
1.30	-1.128309	0.474	0.494	0.032	-0.462	0.462
1.35	-1.134734	0.454	0.520	0.027	-0.493	0.493
1.40	-1.139578	0.432	0.547	0.021	-0.525	0.525
1.45	-1.143303	0.406	0.577	0.017	-0.560	0.560
1.50	-1.146266	0.377	0.610	0.013	-0.597	0.597
1.75	-1.157969	0.202	0.796	0.002	-0.794	0.794
2.00	-1.176176	0.042	0.958	0.000	-0.958	0.958
2.50	-1.236559	0.000	1.000	0.000	-1.000	1.000
3.00	-1.310900	0.000	1.000	0.000	-1.000	1.000
3.5	-1.396067	0.000	1.000	0.000	-1.000	1.000
4.0	-1.487691	0.000	1.000	0.000	-1.000	1.000
5.0	-1.688056	0.000	1.000	0.000	-1.000	1.000

[a]Weight of the ionic structure where negative charge on the H atom placed in the Z<0 direction. [b]Weight of the ionic structure where negative charge on the Cl atom placed in the Z>0 direction. [c]Charge corresponds to the H atom placed in the Z<0 direction. [d]Charge corresponds to the Cl atom placed in the Z>0 direction.

Table S21. Dependence of total energies (E, -459.0 au), weights of the covalent and ionic structures, and VB Mulliken charges of the atoms, on the H-Cl bond length (Å); calculated with VBSCF/6-311G(d,p) level of theory at F_Z=+0.11 au.

		Weights of the VB structures			VB charges	
R	E	H· ·Cl	H^{-} ^{+}Cl[a]	H^{+} ^{-}Cl[b]	H[c]	Cl[d]
1.10	-1.188926	0.546	0.002	0.451	0.449	-0.449
1.15	-1.209591	0.527	0.000	0.473	0.473	-0.473
1.20	-1.224468	0.507	0.000	0.493	0.498	-0.498
1.25	-1.234940	0.486	0.000	0.514	0.524	-0.524
1.30	-1.242085	0.463	0.000	0.537	0.551	-0.551
1.35	-1.246743	0.438	0.000	0.562	0.578	-0.578
1.40	-1.249576	0.413	0.000	0.587	0.606	-0.606
1.45	-1.251104	0.386	0.000	0.614	0.633	-0.633
1.50	-1.251746	0.359	0.000	0.641	0.661	-0.661
1.75	-1.251270	0.213	0.000	0.787	0.799	-0.799
2.00	-1.258274	0.086	0.000	0.914	0.917	-0.917
2.50	-1.306881	0.000	0.000	1.000	1.000	-1.000
3.00	-1.377062	0.000	0.000	1.000	1.000	-1.000

[a] Weight of the ionic structure where negative charge on the H atom placed in the Z<0 direction. [b] Weight of the ionic structure where negative charge on the Cl atom placed in the Z>0 direction. [c] Charge corresponds to the H atom placed in the Z<0 direction. [d] Charge corresponds to the Cl atom placed in the Z>0 direction.

Table S22. Dependence of total energies (E, -459.0 au) and Mulliken charges of the atoms on the H-Cl bond length (Å) for the covalent and the H^{+} ^{-}Cl ionic-structures of HCl molecule; calculated with VBSCF/6-311G(d,p) level of theory at F_Z=+0.11 au.

	H· ·Cl structure			H^{+} ^{-}Cl structure		
		VB charges			VB charges	
R	E	H[a]	Cl[b]	E	H[a]	Cl[b]
1.10	-1.155022	0.000	0.000	-1.044808	1.000	-1.000
1.15	-1.166308	0.000	0.000	-1.071531	1.000	-1.000
1.20	-1.170502	0.000	0.000	-1.093460	1.000	-1.000
1.25	-1.169270	0.000	0.000	-1.111753	1.000	-1.000
1.30	-1.164057	0.000	0.000	-1.127263	1.000	-1.000
1.35	-1.156089	0.000	0.000	-1.140619	1.000	-1.000
1.40	-1.146382	0.000	0.000	-1.152292	1.000	-1.000
1.45	-1.135744	0.000	0.000	-1.162637	1.000	-1.000
1.50	-1.124695	0.000	0.000	-1.171936	1.000	-1.000
1.75	-1.076643	0.000	0.000	-1.208962	1.000	-1.000
2.00	-1.046331	0.000	0.000	-1.239616	1.000	-1.000
2.50	-1.019908	0.000	0.000	-1.303209	1.000	-1.000
3.00	-1.012352	0.000	0.000	-1.377034	1.000	-1.000

[a] Charge corresponds to the H atom placed in the Z<0 direction. [b] Charge corresponds to the Cl atom placed in the Z>0 direction.

Table S23. F_Z (au) dependence of total energies (E, -616.0 au), weights of the covalent- and ionic structures and VB Mulliken charges of the atoms, for Me$_3$CCl; calculated with VBSCF/6-311G(d,p) level of theory. At each F_Z value the B3LYP/cc-pVTZ optimized geometry was used.

		Weights of the VB structures			VB charges		
F_Z	E	Me$_3$C· ·Cl	Me$_3$C$^-$ $^+$Cl^a	Me$_3$C$^+$ $^-$Cl^b	C^c	Me$_3$C	Cl^d
0.0	-0.279754	0.633	0.061	0.307	-0.081	0.221	-0.221
-0.01	-0.272266	0.655	0.080	0.265	-0.069	0.148	-0.148
-0.02	-0.270839	0.669	0.101	0.230	-0.084	0.081	-0.081
-0.03	-0.275661	0.677	0.122	0.201	-0.071	0.015	-0.015
-0.04	-0.286878	0.681	0.144	0.175	-0.060	-0.049	0.049
-0.05	-0.304863	0.682	0.168	0.150	-0.018	-0.114	0.114
-0.06	-0.329901	0.678	0.194	0.127	0.021	-0.179	0.179
-0.07	-0.362550	0.671	0.225	0.104	0.019	-0.247	0.247
-0.08	-0.403341	0.658	0.263	0.079	0.002	-0.319	0.319
-0.09	-0.451426	0.631	0.329	0.040	-0.056	-0.407	0.407
-0.10	dissoc^e						
-0.12^f	-0.689120	0.448	0.540	0.012	-0.135	-0.703	0.703
0.01	-0.293494	0.597	0.040	0.363	-0.086	0.308	-0.308
0.02	-0.313648	0.521	0.018	0.460	-0.077	0.435	-0.435
0.025	-0.326292	0.349	0.001	0.650	-0.012	0.645	-0.645
0.03^g	-0.345687	0.298	0.000	0.702	-0.003	0.699	-0.699
0.03	dissoc^e						

[a] Weight of the ionic structure where negative charge on the C atom placed in the Z<0 direction. [b] Weight of the ionic structure where negative charge on the Cl atom placed in the Z>0 direction. [c] Charge corresponds to the C atom placed in the Z<0 direction. [d] Charge corresponds to the Cl atom placed in the Z>0 direction. [e] At this electric filed molecule is dissociated to the ions. [f] VB calculation with F_Z =-0.12 au was done with optimized geometry obtained with F_Z =-0.09 au. [g] VB calculation with F_Z =+0.03 au was done with optimized geometry obtained with F_Z =+0.025 au.

Table S24. Dependence of total energies (E, -615.0 au), weights of the covalent and ionic structures and VB Mulliken charges of the atoms, on the C-Cl bond length (Å) in Me$_3$CCl; calculated with VBSCF/6-311G(d,p) level of theory at F_Z=-0.02 au. At each R value the B3LYP/cc-pVTZ optimized geometry was used.

		Weights of the VB structures			VB charges		
R	E	Me$_3$C· ·Cl	Me$_3$C$^-$ $^+$Cl^a	Me$_3$C$^+$ $^-$Cl^b	C^c	Me$_3$C	Cl^d
1.70	-1.264437	0.659	0.116	0.225	-0.046	0.044	-0.044
1.75	-1.268758	0.663	0.109	0.228	-0.048	0.061	-0.061
1.80	-1.270695	0.668	0.103	0.230	-0.059	0.076	-0.076
1.85	**-1.270757**	0.673	0.096	0.232	-0.058	0.089	-0.089
1.90	-1.269378	0.678	0.089	0.233	-0.070	0.102	-0.102
1.95	-1.266873	0.685	0.082	0.233	-0.069	0.113	-0.113
2.00	-1.263494	0.691	0.076	0.233	-0.071	0.123	-0.123
2.05	-1.259508	0.699	0.070	0.232	-0.084	0.131	-0.131
2.10	-1.255069	0.706	0.064	0.230	-0.084	0.139	-0.139
2.15	-1.250320	0.714	0.058	0.228	-0.086	0.145	-0.145

2.5	-1.215334	0.788	0.027	0.185	-0.124	0.146	-0.145
3.0	-1.180949	0.935	0.008	0.057	-0.187	0.046	-0.046
3.5	-1.170471	0.991	0.002	0.009	-0.194	0.007	-0.007
4.0	-1.168154	0.998	0.000	0.002	-0.189	0.001	-0.001
5.0	-1.167338	1.000	0.000	0.000	-0.184	0.000	0.000
6.0	-1.167394	1.000	0.000	0.000	-0.171	0.000	0.000

[a] Weight of the ionic structure where negative charge on the atom placed in the Z<0 direction. [b] Weight of the ionic structure where negative charge on the atom placed in the Z>0 direction. [c] Charge corresponds to the atom placed in the Z<0 direction. [d] Charge corresponds to the atom placed in the Z>0 direction.

Table S25. Dependence of total energies (E, -616.0 au), weights of the covalent and ionic structures and VB Mulliken charges of the atoms on the C-Cl bond length (Å) for Me_3CCl molecule calculated with VBSCF/6-311G(d,p) level of theory at F_Z=+0.02 au. At each R value the B3LYP/cc-pVTZ optimized geometry was used.

		Weights of the VB structures			VB charges		
R	E	$Me_3C\cdot\ \cdot Cl$	$Me_3C^{-}\ {}^{+}Cl$[a]	$Me_3C^{+}\ {}^{-}Cl$[b]	C[c]	Me_3C	Cl[d]
1.70	-0.298497	0.599	0.058	0.343	-0.098	0.275	-0.275
1.75	-0.305094	0.590	0.050	0.360	-0.090	0.300	-0.300
1.80	-0.309488	0.581	0.043	0.377	-0.082	0.325	-0.325
1.85	-0.312185	0.569	0.036	0.395	-0.076	0.350	-0.350
1.90	-0.313580	0.556	0.030	0.414	-0.070	0.376	-0.376
1.95	-0.314009	0.541	0.024	0.435	-0.063	0.403	-0.403
2.00	-0.313747	0.523	0.019	0.458	-0.055	0.432	-0.432
2.05	-0.313013	0.503	0.014	0.483	-0.046	0.462	-0.462
2.10	-0.311988	0.479	0.010	0.511	-0.036	0.494	-0.494
2.15	-0.310822	0.451	0.007	0.542	-0.023	0.528	-0.528
2.5	-0.305841	0.208	0.000	0.793	0.083	0.790	-0.790
3.0	-0.309657	0.044	0.000	0.956	0.128	0.954	-0.954
3.5	-0.314260	0.000	0.000	1.000	0.112	0.986	-0.986

[a] Weight of the ionic structure where negative charge on the atom placed in the Z<0 direction. [b] Weight of the ionic structure where negative charge on the atom placed in the Z>0 direction. [c] Charge corresponds to the atom placed in the Z<0 direction. [d] Charge corresponds to the atom placed in the Z>0 direction.

CASSCF: CASSCF calculations were carried out with Gaussian 09.

The n=2 Level for H was calculated with CASSCF(1,5)/daug-cc-pV6Z/OEEF,

a)

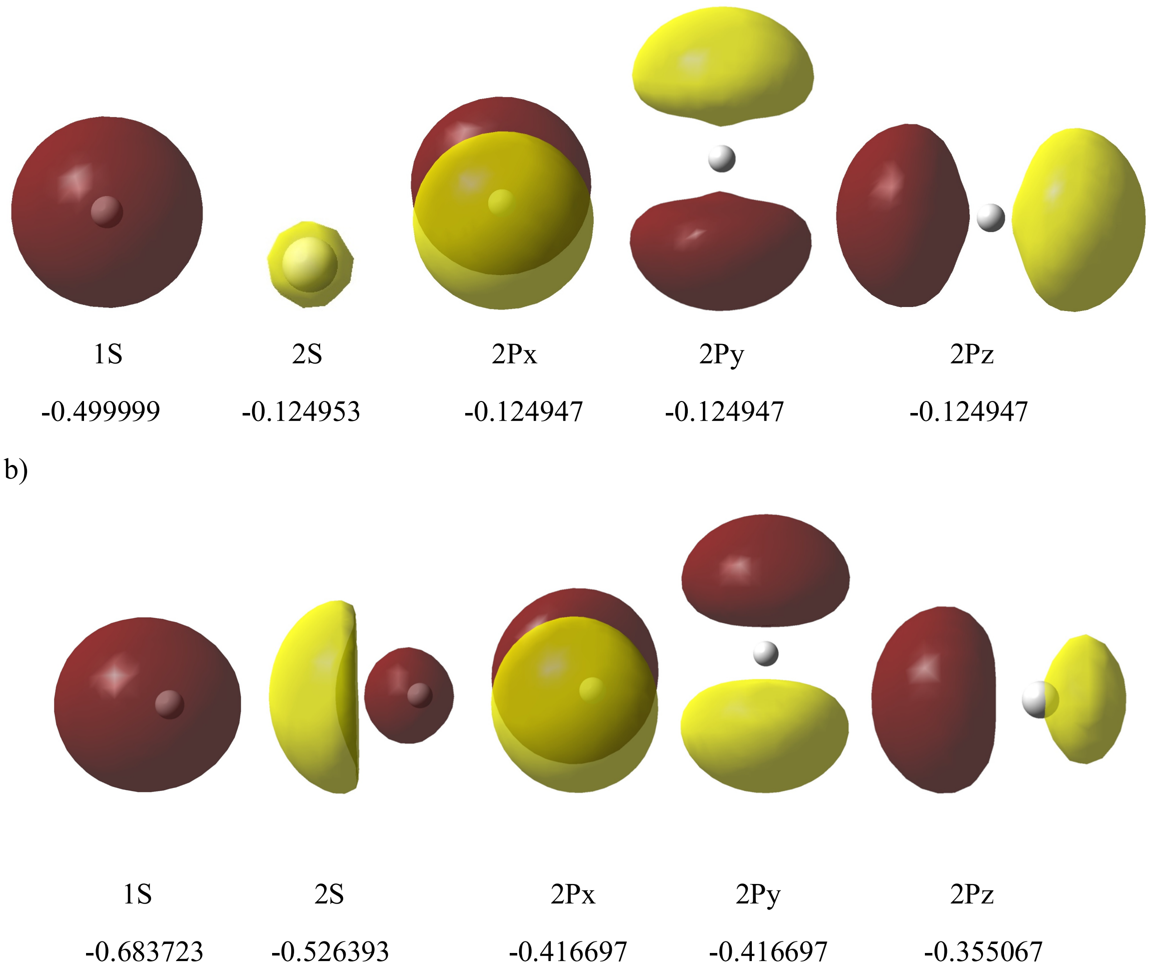

Figure S2. Shape of 1S, 2S, 2Px, 2Py, 2Pz AO's of H atom and the energies of the corresponding states with F_Z=0.0 (a) and F_Z=+0.1 au (b) in the Z-direction calculated by CASSCF(1,5)/daug-cc-pV6Z level of theory. Note the forbidden mixing is removed.

Rotational Barrier for $H_2C{=}CH_2$: The rotational barrier (kcal mol^{-1}) for $H_2C{=}CH_2$ was calculated using B3LYP with cc-PCTZ and cc-pVQZ basis sets as well as with CASSCF(2,2) and CASSCF(12,13) with cc-pVTZ basis set using the F_Z values in Table S26. Z is along the C=C axis.

Table S26. Dependence of the barrier of rotation ΔE_{rot} (kcal mol^{-1}) on F_Z (au); calculated by B3LYP functional with different basis sets and with different CASSCF levels with cc-pVTZ basis set

	B3LYP		CASSCF	
F_Z	cc-pVTZ	cc-pVQZ	CAS(2/2)	CAS(12,13)[a]
0.0	63.87	63.77	66.36	69.56

0.0125	64.05	63.92	66.60	69.79
0.0250	65.54	64.32	67.26	70.48
0.0500	65.68	64.98	71.37	73.80

[a] With geometry from B3LYP/cc-pVTZ optimization

I. References for Methodology

[S1] *Gaussian 09*, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

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II. Literature on EEF & Electrostatics

1. Sources for Electrostatics: The book by Coulson[S4] is a highly didactic mathematical treatise of the topic of electricity, including its history from the experiment of Thales of Miletus onwards. Page 11-72 deals with aspects of electrostatics theory.

The multipole expression for interaction of a molecular species with a uniform field, can be derived from the expression of the induced dipole-moment ($\mu_{ind,Z}$) as a function of the field strength F_Z in a given direction:[S5]

$$\mu_{ind,Z} = -dE/dF_Z \qquad \text{(S1)}$$

$\mu_{ind,Z}$ is given as a Taylor series of terms, which include the dipole moment, μ_0, (for F=0), the polarisability term, αF, which depends on the F, the hyperpolarisability which depends on βF^2, etc. As we show in the text, the size of $\mu_{ind,Z}$ for the TS is much larger than μ_0, and this increase is caused by increasing mixing of ionic and charge-transfer states into the wave function of the TS.

The interaction energy of the induced dipole with the field, is then the direct product, $\mu_{ind,Z} \cdot F_Z$ (see eq. B.5 in Textbox 1).[S5]

References for Electrostatics

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[S5] W. A. Atkins, *Quanta. A Handbook of Concepts,* Oxford University Press, New York, 1991, page 282. See also for example refs. 2 and 6, in (A) in the list below.

2. Additional References: Since the tutorial is limited to 50 references, we decided to include a list of the literature, which we read in preparation of the tutorial. This list is sub-classified below by topics.

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