A theoretical study of the activation of nitromethane under applied electric fields

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F/a.u.	0.00	0.01	0.02	0.03	0.04	0.05
R(1,2)	1.089	1.088	1.089	1.089	1.090	1.092
R(1,3)	1.092	1.092	1.093	1.094	1.096	1.099
R(1,4)	1.089	1.088	1.089	1.089	1.090	1.092
R(1,5)	1.500	1.500	1.500	1.500	1.500	1.500
R(5,6)	1.217	1.220	1.223	1.227	1.230	1.235
R(5,7)	1.217	1.220	1.223	1.227	1.230	1.235
A(2,1,3)	110.780	110.642	110.462	110.224	109.906	109.473
A(2,1,4)	112.888	112.903	112.932	112.948	112.993	113.059
A(2,1,5)	107.735	107.810	107.914	108.065	108.293	108.541
A(3,1,4)	110.780	110.641	110.462	110.224	109.906	109.423
A(3,1,5)	106.630	106.761	106.909	107.095	107.311	107.601
A(4,1,5)	107.735	107.810	107.914	108.066	108.296	108.541
A(1,5,6)	117.100	117.713	118.352	119.008	119.657	120.342
A(1,5,7)	117.100	117.713	118.352	119.008	119.657	120.342
A(6,5,7)	125.768	124.548	123.234	121.966	120.612	119.304
D(2,1,5,6)	152.013	151.969	151.986	152.025	152.090	152.226
D(2,1,5,7)	-29.941	-29.792	-29.652	-29.493	-29.258	-28.981
D(3,1,5,6)	-89.023	-89.120	-89.181	-89.241	-89.326	-89.397
D(3,1,5,7)	89.023	89.120	89.181	89.241	89.326	89.397
D(4,1,5,6)	29.941	29.792	29.652	29.493	29.258	28.981
D(4,1,5,7)	-152.013	-151.969	-151.985	-152.025	-152.090	-152.226

Table S2 Geometric parameters of NM in singlet state at the equilibrium C–N bond lengths (r_{C-N} =1.5Å) under different field strengths of 0.00, 0.01, 0.02, 0.03, 0.04, 0.05 a.u. in the –x direction.

F/a.u.	0.00	-0.01	-0.02	-0.03	-0.04	-0.05
R(1,2)	1.089	1.089	1.090	1.092	1.094	1.093
R(1,3)	1.092	1.092	1.093	1.094	1.096	1.094
R(1,4)	1.089	1.089	1.090	1.092	1.094	1.093
R(1,5)	1.500	1.500	1.500	1.500	1.500	1.500
R(5,6)	1.217	1.215	1.213	1.210	1.207	1.204
R(5,7)	1.217	1.215	1.213	1.210	1.207	1.204
A(2,1,3)	110.780	110.878	110.944	111.000	111.102	111.297
A(2,1,4)	112.888	112.830	112.765	112.653	112.521	111.949
A(2,1,5)	107.735	107.714	107.712	107.756	107.762	107.889
A(3,1,4)	110.780	110.878	110.944	111.000	111.102	111.297
A(3,1,5)	106.630	106.520	106.454	106.366	106.276	106.234
A(4,1,5)	107.735	107.714	107.712	107.757	107.762	107.889
A(1,5,6)	117.100	116.476	115.932	115.363	114.740	113.724
A(1,5,7)	117.100	116.476	115.933	115.363	114.740	113.724
A(6,5,7)	125.768	127.012	128.082	129.206	130.448	132.493
D(2,1,5,6)	152.013	152.011	152.158	152.259	152.215	151.786
D(2,1,5,7)	-29.941	-30.032	-30.260	-30.444	-30.551	-30.662
D(3,1,5,6)	-89.023	-88.978	-88.791	-88.648	-88.617	-88.776
D(3,1,5,7)	89.023	88.979	88.791	88.648	88.617	88.776
D(4,1,5,6)	29.941	30.032	30.260	30.444	30.551	30.662
D(4,1,5,7)	-152.013	-152.011	-152.158	-152.259	-152.215	-151.786

Table S3 Energy of singlet and triplet NM in presence of an external field in the +x direction.

F/a.u.	0.00		0.01		0.02		0.03	
r(C-N)/Å	S	T	S	T	S	T	S	T
1.3	17.066		17.038		18.731		17.244	
1.35	8.665		8.704		10.440		9.0641	
1.4	3.518		3.568		3.7134		3.931	
1.45	0.829		0.859		2.477		1.102	
1.5	0.000		0.000		0.000		0.000	
1.55	0.556		0.506		1.788		0.391	
1.6	2.126		2.018		1.740		1.295	
1.7	7.219		7.014		6.360		5.274	
1.8	13.656		13.412		12.333		10.483	
1.9	20.454		20.260		18.771		16.062	
2.0	27.015		26.995		25.143		21.493	
2.1	32.989		33.285		31.165		26.545	
2.2	38.205		38.967		36.731		31.085	
2.3	47.100		43.960		41.802		35.078	
2.4	52.979		48.218		46.408		38.532	
2.5	55.824	66.827	58.144	75.111	50.572	83.082	41.440	90.416
2.6	57.591	65.055	61.440	73.478	54.338	81.468	43.812	89.231
2.7	58.689	63.760	63.774	72.281	57.732	80.785	45.658	89.695
2.8	59.395	62.834	65.426	71.411	60.800	79.993	46.990	87.596
2.9	59.876	62.175	66.609	70.800	63.572	78.885	47.835	86.933
3.0	60.225	61.729	67.480	70.143	66.071	78.511	48.225	86.847
3.1	60.493	61.407	68.134	70.118	68.334	78.188	48.201	86.912
3.2	60.712	61.200	68.644	69.926	70.359	78.115	47.809	86.454
3.3	60.896	61.072	69.053	69.782	72.152	78.132	47.090	86.430
3.4	61.054	61.014	69.393	69.710	73.693	77.936	46.104	86.401
3.5	61.193	61.001	69.688	69.669	74.961	77.883	44.877	86.349
3.6	61.318	61.018	69.954	69.517	75.931	77.891	43.449	86.269
3.7	61.430	61.055	70.187	69.591	76.578	77.860	41.846	86.204
3.8	61.533	61.105	70.431	69.573	76.903	77.857	40.105	86.148
3.9	61.626	61.174	70.682	69.549	76.942	77.874	38.208	86.081
4.0	61.712	61.223	71.791	69.517	76.721	77.901	36.178	86.027

Table S4 Energy of singlet NM in presence of an external field in the +x direction.

F/a.u. r(C-N)/Å	0.00	0.01	0.02	0.03	0.04	0.05
1.3	17.071	-1.432	-3.642	-19.504	-36.016	-54.677
1.35	8.669	-6.567	-11.932	-27.683	-44.065	-62.562
1.4	3.522	-9.276	-18.660	-32.817	-49.178	-67.929
1.45	0.834	-10.136	-19.896	-35.646	-52.090	-70.641
1.5	0.004	-9.630	-22.373	-36.748	-53.356	-72.360
1.55	0.56	-8.117	-20.585	-36.357	-53.430	-72.469
1.6	2.13	-3.122	-20.633	-35.452	-52.652	-72.344
1.7	7.223	3.276	-16.013	-31.474	-49.533	-70.271
1.8	13.66	10.125	-10.039	-26.265	-45.409	-67.517
1.9	20.458	16.859	-3.602	-20.686	-41.114	-64.855
2.0	27.019	23.150	2.771	-15.254	-37.122	-62.726
2.1	32.994	28.831	8.793	-10.203	-33.697	-61.337
2.2	38.21	33.824	14.358	-5.662	-30.932	-60.752
2.3	47.104	38.082	19.430	-1.669	-28.868	-60.935
2.4	52.983	48.008	24.035	1.784	-27.492	-61.808
2.5	55.828	51.304	28.199	4.693	-26.754	-63.286
2.6	57.596	53.639	31.966	7.064	-26.618	-65.285
2.7	58.694	55.291	35.359	8.910	-27.018	-67.712
2.8	59.4	56.473	38.427	10.242	-27.894	-70.503
2.9	59.88	57.345	41.199	11.087	-29.184	-73.608
3.0	60.229	57.998	43.698	11.477	-30.823	-57.724
3.1	60.498	58.508	45.962	11.453	-32.790	-80.562
3.2	60.716	58.918	47.986	11.061	-35.009	-89.059
3.3	60.900	59.257	49.779	10.342	-37.447	-88.287
3.4	61.058	59.552	51.320	9.356	-40.080	-92.378
3.5	61.197	59.818	52.589	8.129	-42.877	-103.036
3.6	61.322	60.052	53.558	6.7009	-48.848	-110.593

Table S5 Energy of singlet and triplet NM in presence of an external field in the -x direction.

F/a.u.	0.00		-0.01		-0.02		-0.03	
r(C-N)/Å	S	T	S	T	S	T	S	T
1.3	17.066		17.220		17.597		18.261	
1.35	8.665		8.773		9.083		9.656	
1.4	3.518		3.580		3.815		4.253	
1.45	0.829		0.859		0.998		1.249	
1.5	0.000		0.000		0.000		0.000	
1.55	0.556		0.493		0.342		0.025	
1.6	2.126		2.000		1.638		0.912	
1.7	7.219		6.881		5.938		4.142	
1.8	13.656		12.966		11.233		8.103	
1.9	20.454		19.276		16.610		12.033	
2.0	27.015		25.239		21.607		15.656	
2.1	32.989		30.555		26.070		18.946	
2.2	38.205		35.141		29.987		21.947	
2.3	47.100		45.441		33.410		24.718	
2.4	52.979		48.646		36.376		27.273	
2.5	55.824	66.827	50.550	64.311	38.943	56.126	29.632	41.596
2.6	57.591	65.055	51.649	60.964	41.046	52.620	31.826	39.606
2.7	58.689	63.760	52.266	58.422	42.774	49.976	33.842	38.074
2.8	59.395	62.834	52.638	56.516	44.145	48.000	36.183	36.698
2.9	59.876	62.175	52.869	55.129	45.166	46.519	38.875	35.595
3.0	60.225	61.729	53.025	54.110	45.929	45.641	39.377	34.707
3.1	60.493	61.407	53.141	53.362	46.467	44.470	37.785	34.568
3.2	60.712	61.200	53.235	52.800	46.795	43.748	36.162	33.561
3.3	60.896	61.072	53.311	51.844	46.926	42.481	34.515	33.033
3.4	61.054	61.014	53.379	51.633	46.885	42.192	32.846	32.597
3.5	61.193	61.001	53.440	51.143	46.633	41.925	31.153	32.239
3.6	61.318	61.018	53.498	51.364	46.308	41.732	30.154	32.176

Table S6 Energy of singlet NM in presence of an external field in the -x direction.

F/a.u. r(C-N)/Å	0.00	-0.01	-0.02	-0.03	-0.04	-0.05
1.3	17.071	25.302	31.634	36.025	38.326	34.190
1.35	8.669	16.856	23.120	27.420	29.532	22.592
1.4	3.522	11.663	17.851	22.017	23.845	14.558
1.45	0.834	8.941	15.034	19.013	20.446	10.460
1.5	0.004	8.082	14.037	17.764	18.679	5.300
1.55	0.56	8.575	14.378	17.789	18.028	2.376
1.6	2.13	10.082	15.675	18.677	18.101	1.972
1.7	7.223	14.963	19.974	21.906	19.306	9.265
1.8	13.66	21.048	25.269	25.867	20.931	6.999
1.9	20.458	27.359	30.647	29.797	22.451	4.345
2.0	27.019	33.321	35.643	33.420	23.723	0.869
2.1	32.994	38.637	40.107	36.710	24.682	-4.000
2.2	38.21	43.223	44.024	39.711	25.208	-9.948
2.3	47.104	53.523	47.447	42.482	25.015	-16.031
2.4	52.983	56.728	50.413	45.037	23.550	-21.891
2.5	55.828	58.633	52.979	47.396	21.077	-27.278
2.6	57.596	59.732	55.082	49.590	17.940	-32.753
2.7	58.694	60.348	56.811	51.606	14.566	-40.230
2.8	59.4	60.721	58.181	53.947	11.295	-44.604
2.9	59.88	60.952	59.203	56.639	8.164	-48.774
3.0	60.229	61.107	59.965	57.141	5.160	-52.800
3.1	60.498	61.223	60.504	55.549	2.235	-56.761
3.2	60.716	61.317	60.832	53.926	-0.654	-60.708
3.3	60.900	61.393	60.963	52.279	-3.527	-64.687
3.4	61.058	61.461	60.922	50.610	-9.385	-68.747
3.5	61.197	61.522	60.670	48.917	-9.372	-73.364
3.6	61.322	61.580	60.345	-46.148	-9.436	-77.768

Table S7 Energy of singlet and triplet NM in presence of an external field in the +y direction.

F/a.u.	0.00		0.01		0.02		0.03	
r(C-N)/Å	S	T	S	T	S	T	S	T
1.3	17.066		17.086		17.097		17.109	
1.35	8.665		8.690		8.702		8.726	
1.4	3.518		3.528		3.541		3.564	
1.45	0.829		0.834		0.841		0.856	
1.5	0.000		0.000		0.000		0.000	
1.55	0.556		0.551		0.543		0.525	
1.6	2.126		2.118		2.096		2.055	
1.7	7.219		7.206		7.166		7.086	
1.8	13.656		13.632		13.565		13.440	
1.9	20.454		20.437		20.365		20.211	
2.0	27.015		27.000		26.921		26.740	
2.1	32.989		32.973		32.890		32.699	
2.2	38.205		38.193		38.189		37.933	
2.3	47.100		49.360		49.349		49.157	
2.4	52.979		53.623		53.655		53.520	
2.5	55.824	66.827	56.386	66.674	56.463	66.774	56.397	66.914
2.6	57.591	65.055	58.082	64.837	58.176	64.946	58.164	64.998
2.7	58.689	63.760	58.757	63.535	58.659	63.599	58.607	63.547
2.8	59.395	62.834	59.473	62.596	59.373	62.578	59.312	62.452
2.9	59.876	62.175	59.958	62.828	59.879	62.536	59.958	61.518
3.0	60.225	61.729	60.302	61.466	60.313	62.227	60.313	60.946
3.1	60.493	61.407	60.658	61.148	60.583	61.225	60.528	61.135
3.2	60.712	61.200	60.787	60.900	60.784	60.904	60.728	60.671
3.3	60.896	61.072	60.956	60.787	60.959	60.715	60.876	60.441
3.4	61.054	61.014	61.104	60.725	61.102	60.584	61.021	60.316
3.5	61.193	61.001	61.235	60.697	61.224	60.505	61.130	60.139
3.6	61.318	61.018	61.350	60.671	61.329	60.351	61.222	60.097

Table S8 Energy of singlet NM in presence of an external field in the +y direction.

| F/a.u. r(C-N)/Å	0.00	0.01	0.02	0.03	0.04	0.05
1.3	17.071	15.643	11.337	4.136	-6.039	-19.346
1.35	8.669	7.247	2.942	-4.247	-14.412	-27.698
1.4	3.522	2.085	-2.219	-9.410	-19.572	-32.861
1.45	0.834	-0.609	-4.919	-12.117	-22.291	-35.593
1.5	0.004	-1.443	-5.760	-12.973	-23.168	-36.498
1.55	0.56	-0.892	-5.217	-12.448	-22.671	-36.041
1.6	2.13	0.675	-3.664	-10.918	-21.172	-34.584
1.7	7.223	5.763	1.406	-5.887	-16.220	-29.731
1.8	13.66	12.189	7.805	0.467	-9.919	-23.516
1.9	20.458	18.994	14.605	7.238	-3.217	-16.881
2.0	27.019	25.557	21.161	13.767	3.295	-10.420
2.1	32.994	31.530	27.130	19.726	9.259	-4.496
2.2	38.21	36.750	32.428	24.960	14.501	0.754
2.3	47.104	47.917	43.589	36.183	18.931	5.222
2.4	52.983	52.180	47.895	40.546	23.011	9.467
2.5	55.828	54.943	50.703	43.424	27.405	13.047
2.6	57.596	56.639	52.415	45.191	34.242	20.769
2.7	58.694	57.314	52.899	45.634	35.375	21.958
2.8	59.4	58.030	53.613	46.339	36.093	22.637
2.9	59.88	58.517	54.119	46.985	36.603	23.188
3.0	60.229	58.859	54.553	47.340	36.967	23.553
3.1	60.498	59.215	54.823	47.555	37.219	21.639
3.2	60.716	59.344	55.024	47.755	37.407	22.425
3.3	60.900	59.513	55.199	47.903	37.552	23.445
3.4	61.058	59.661	55.342	48.048	37.665	24.310
3.5	61.197	59.792	55.464	48.157	37.749	25.022
3.6	61.322	59.907	55.569	48.249	37.887	24.583
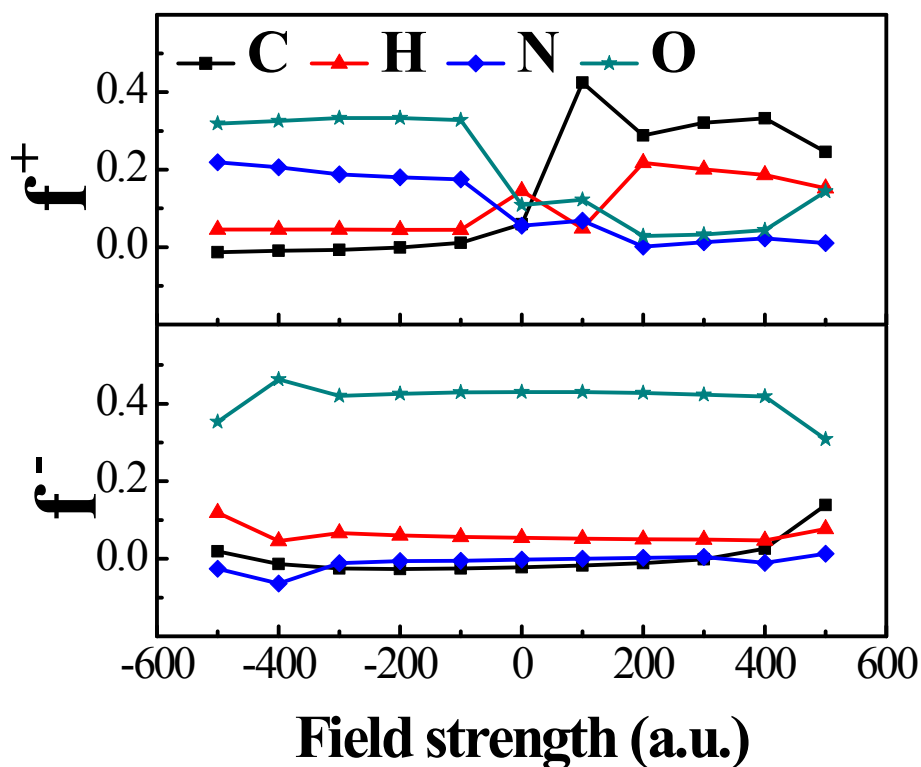
Figure S1 Fukui functions of atom C, H, N, O in nitromethane under electric fields either in the $+x$ or $-x$ direction.

Some of the Fukui functions presented in the Figure are small and negative, which are attributed to orbital relaxation when one electron is added or removed. Negative Fukui functions have been discussed by several authors.[1-4] Our calculations reveal that the orbital relaxation becomes more common in presence of external fields.

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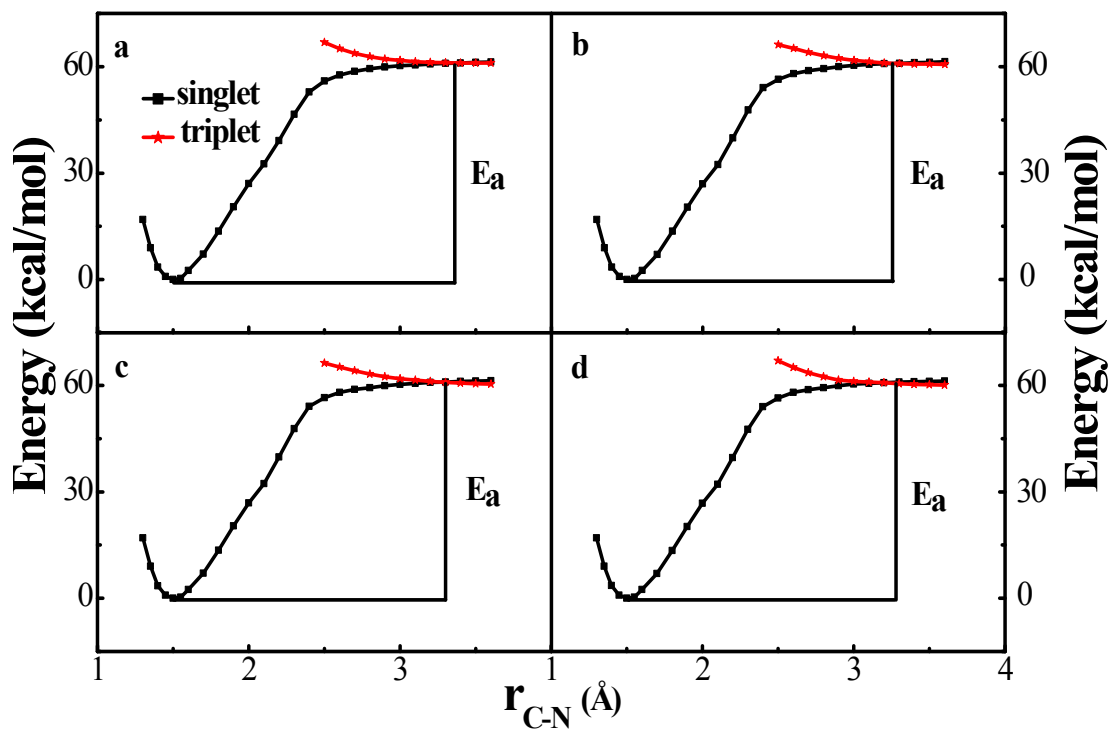
Figure S2 Energy landscapes of NM under electric fields in the +*y* direction. The field strength is 0.00 (a), 0.01 (b), 0.02 (c), and 0.03 au (d).