THEORETICAL MODEL COMPARISON

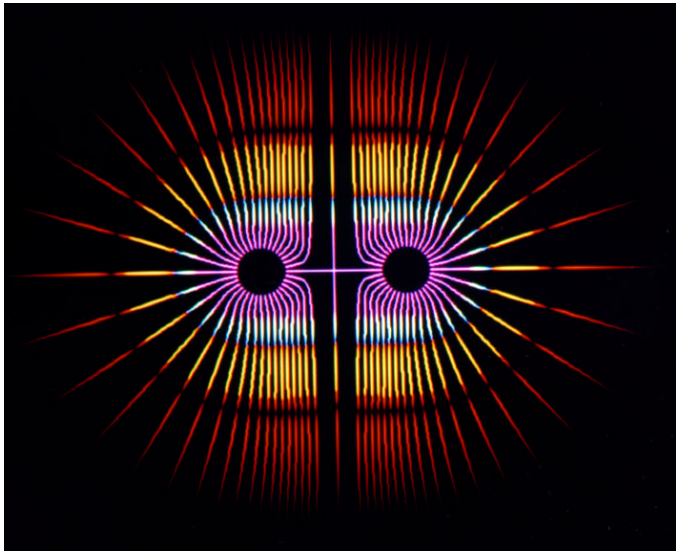
As mentioned in the Method section, we calculated wave function files at both the MP2(full)/6-31G* and RHF/6-31G* levels for CH_3NN^+, HNN^+ and N_2. These two sets of calculations allow one to employ *CCGVF* to visually compare theoretical models with and without electron correlation effects. The restricted Hartree-Fock (RHF) model neglects important electron correlation effects and the full second order Møller-Plesset (MP2(full)) perturbation theory includes some electron correlation. Using *CCGVF* and the density values calculated by *Gaussian92*, the differences between the theoretical models become apparent. As compared to the RHF level, the MP2(full) level gradient vector lines show a higher degree of isotropy close to the atom cores and also a more moderate anisotropy in the bonding regions. The color coding also shows electron correlation to shift electron density out of the bonding regions and into the core regions.

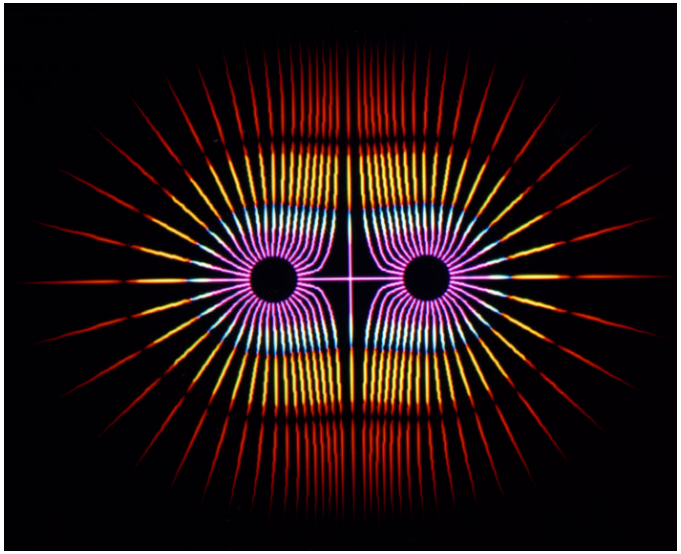
Electron Correlation Effects on Density Color-Coded Gradient Vector Fields

Uncorrelated RHF/6-31G*

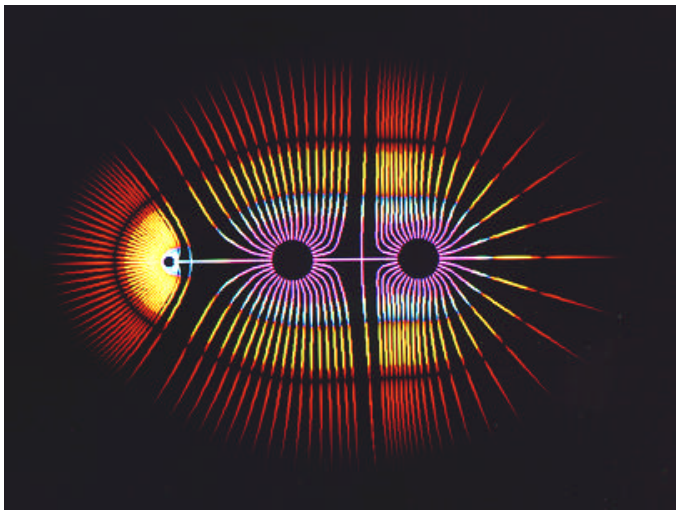
Correlated MP2(full)/6-31G*

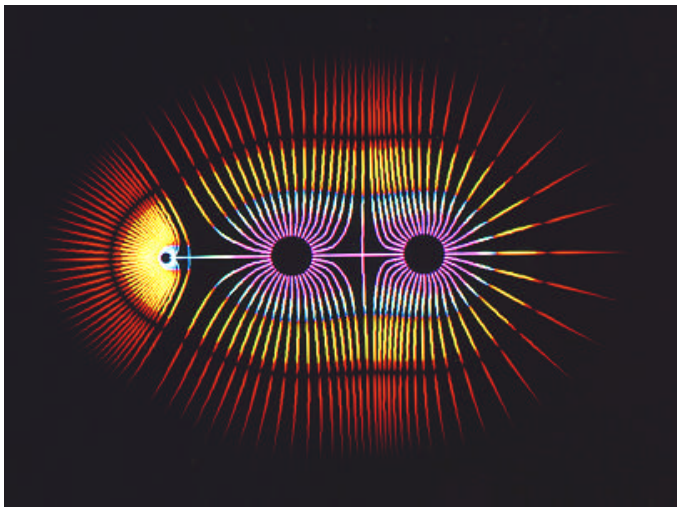
N≡N



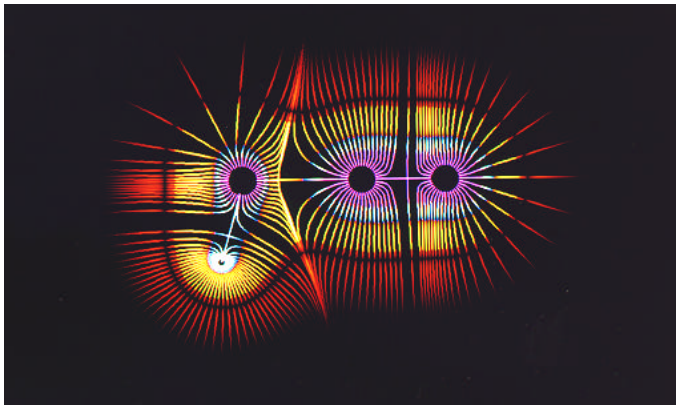


[H—N≡N]$^{+}$





[Me—N≡N]$^{+}$



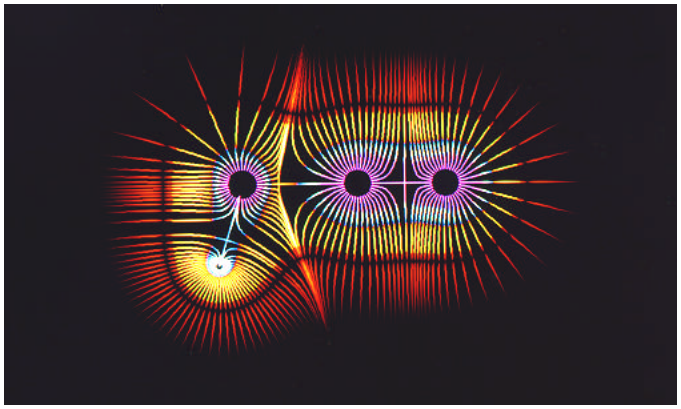


Table 1. Physical data of CH_3NN^+, HNN^+ and N_2.

Molecule	Method	Atom A	Atom B	R_A	R_B	ρ
N_2	RHF	N	N	1.019	1.019	0.711
	MP2	*N*	*N*	*1.068*	*1.068*	*0.620*
HNN^+	RHF	N	N	1.107	0.917	0.688
	MP2			*1.136*	*0.986*	*0.597*
		N	H	1.594	0.344	0.285
				1.601	*0.368*	*0.270*
CH_3NN^+	RHF	N	N	1.107	0.920	0.690
	MP2			*1.142*	*0.989*	*0.592*
		N	C	1.990	0.863	0.171
				1.894	*0.866*	*0.204*
		C	H	1.376	0.662	0.294
				1.398	*0.665*	*0.277*

(a) R_A and R_B are the distances from atoms A and B to the critical point in atomic units and ρ is the magnitude of the electron density.