Supporting Supplementary Information for *Impact of the Kohn-Sham Delocalization Error on Organic Conjugated π Systems*

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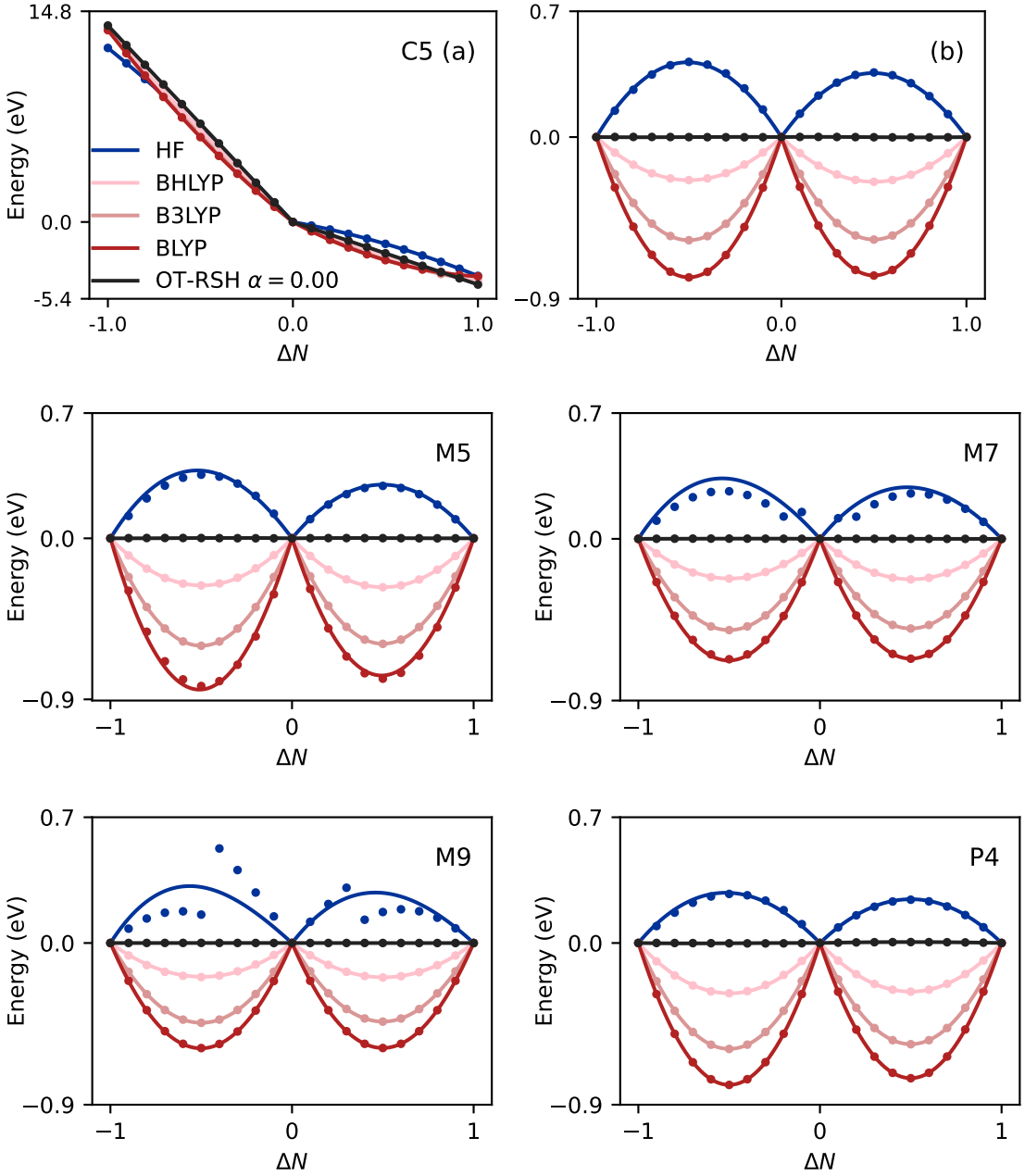
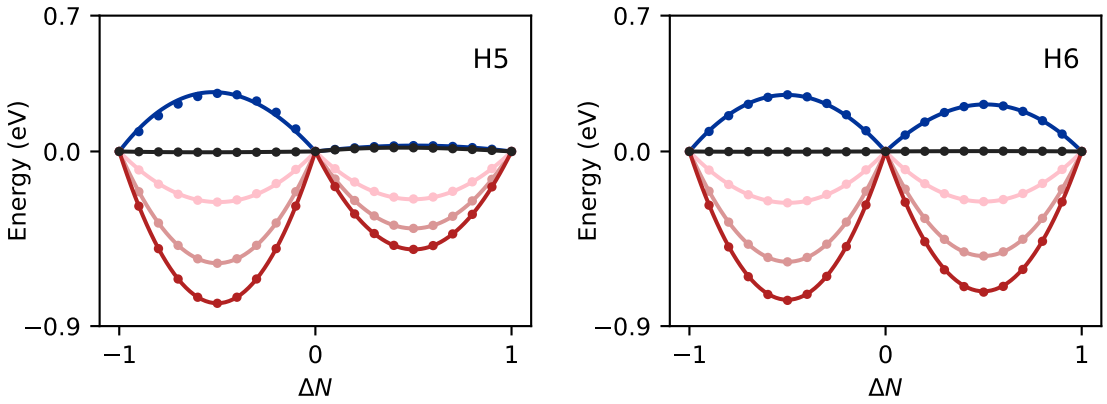
Sections included in this document:

S1 Fractional occupation calculation




H5
H6
Energy (eV)
0.7
0.0
−0.9
−1
0
1
ΔN

S2 Optimal Tuning and Curvature Data

Tab. S1 Optimal parameters for IP tuning ($k = 0$ only in the J^2 definition).

Molecule	$\gamma_{\alpha=0.00}$	$J^2_{\alpha=0.00}$	$\gamma_{\alpha=0.25}$	$J^2_{\alpha=0.25}$
C5	0.330	1.3e-07	0.249	6.6e-11
C7	0.280	4.0e-07	0.209	2.7e-09
C9	0.250	2.3e-09	0.180	5.5e-09
M5	0.349	1.4e-09	0.266	7.7e-10
M7	0.301	5.6e-09	0.227	8.6e-10
M9	0.267	6.1e-10	0.199	5.0e-09
P4	0.330	6.2e-09	0.250	3.3e-06
P6	0.290	1.2e-09	0.220	3.9e-07
P8	0.260	1.2e-09	0.200	3.2e-07
H5	0.300	6.1e-07	0.239	3.0e-10
H6	0.310	2.6e-09	0.240	5.8e-07
H8	0.270	2.3e-07	0.214	1.7e-09
H10	0.270	3.1e-07	0.202	1.2e-10

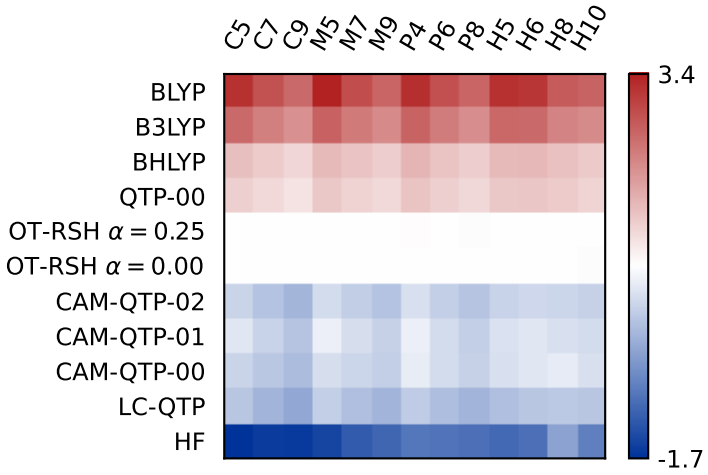


Fig. S1 $E(N)$ curvature (eV) for the ΔN interval $[-1, 0]$ for the set of molecules and the range of functionals tested in this work. OT-RSH data based on IP tuning ($k = 0$ only).

Tab. S2 HF, BHLYP, B3LYP, BLYP, QTP functional curvatures

			CAM-							
	ΔN	QTP-00	QTP-00	QTP-01	QTP-02	LC-QTP	HF	BHLYP	B3LYP	BLYP
C5	$[-1,0]$	0.73	-0.34	-0.20	-0.35	-0.46	-1.67	0.96	2.30	3.12
	$[0,+1]$	0.78	-0.29	-0.20	-0.34	-0.47	-1.43	1.00	2.28	3.08
C7	$[-1,0]$	0.56	-0.44	-0.36	-0.49	-0.60	-1.60	0.77	1.93	2.63
	$[0,+1]$	0.57	-0.43	-0.36	-0.48	-0.60	-1.53	0.77	1.92	2.60
C9	$[-1,0]$	0.43	-0.54	-0.48	-0.60	-0.71	-1.61	0.62	1.68	2.30
	$[0,+1]$	0.42	-0.55	-0.48	-0.60	-0.71	-1.65	0.61	1.67	2.28
M5	$[-1,0]$	0.82	-0.26	-0.12	-0.27	-0.39	-1.51	1.05	2.40	3.38
	$[0,+1]$	0.88	-0.19	-0.12	-0.25	-0.37	-1.20	1.09	2.36	3.06
M7	$[-1,0]$	0.68	-0.33	-0.27	-0.40	-0.51	-1.34	0.88	2.03	2.71
	$[0,+1]$	0.71	-0.28	-0.26	-0.37	-0.49	-1.15	0.90	2.00	2.67
M9	$[-1,0]$	0.57	-0.39	-0.37	-0.48	-0.60	-1.25	0.75	1.78	2.34
	$[0,+1]$	0.59	-0.35	-0.35	-0.46	-0.57	-1.12	0.76	1.75	2.34
P4	$[-1,0]$	0.91	-0.16	-0.13	-0.25	-0.41	-1.12	1.12	2.36	3.16
	$[0,+1]$	0.89	-0.15	-0.16	-0.28	-0.42	-0.98	1.08	2.25	3.01
P6	$[-1,0]$	0.72	-0.28	-0.28	-0.39	-0.53	-1.14	0.91	1.99	2.67
	$[0,+1]$	0.72	-0.25	-0.28	-0.38	-0.51	-1.00	0.90	1.93	2.58
P8	$[-1,0]$	0.58	-0.37	-0.38	-0.48	-0.61	-1.16	0.76	1.74	2.33
	$[0,+1]$	0.60	-0.33	-0.37	-0.46	-0.58	-1.03	0.76	1.71	2.28
H5	$[-1,0]$	0.83	-0.25	-0.24	-0.36	-0.51	-1.22	1.04	2.30	3.13
	$[0,+1]$	0.89	0.20	0.06	0.05	0.02	-0.12	0.99	1.59	2.02
H6	$[-1,0]$	0.86	-0.21	-0.20	-0.31	-0.46	-1.17	1.06	2.28	3.06
	$[0,+1]$	0.85	-0.17	-0.20	-0.30	-0.41	-0.97	1.03	2.16	2.88
H8	$[-1,0]$	0.77	-0.17	-0.26	-0.33	-0.43	-0.74	0.93	1.89	2.48
	$[0,+1]$	0.80	0.17	0.04	0.03	0.01	-0.11	0.89	1.44	1.82
H10	$[-1,0]$	0.65	-0.26	-0.29	-0.37	-0.47	-1.04	0.81	1.76	2.36
	$[0,+1]$	0.66	-0.22	-0.26	-0.34	-0.42	-0.89	0.82	1.73	2.31

Tab. S3 OT-RSH curvatures

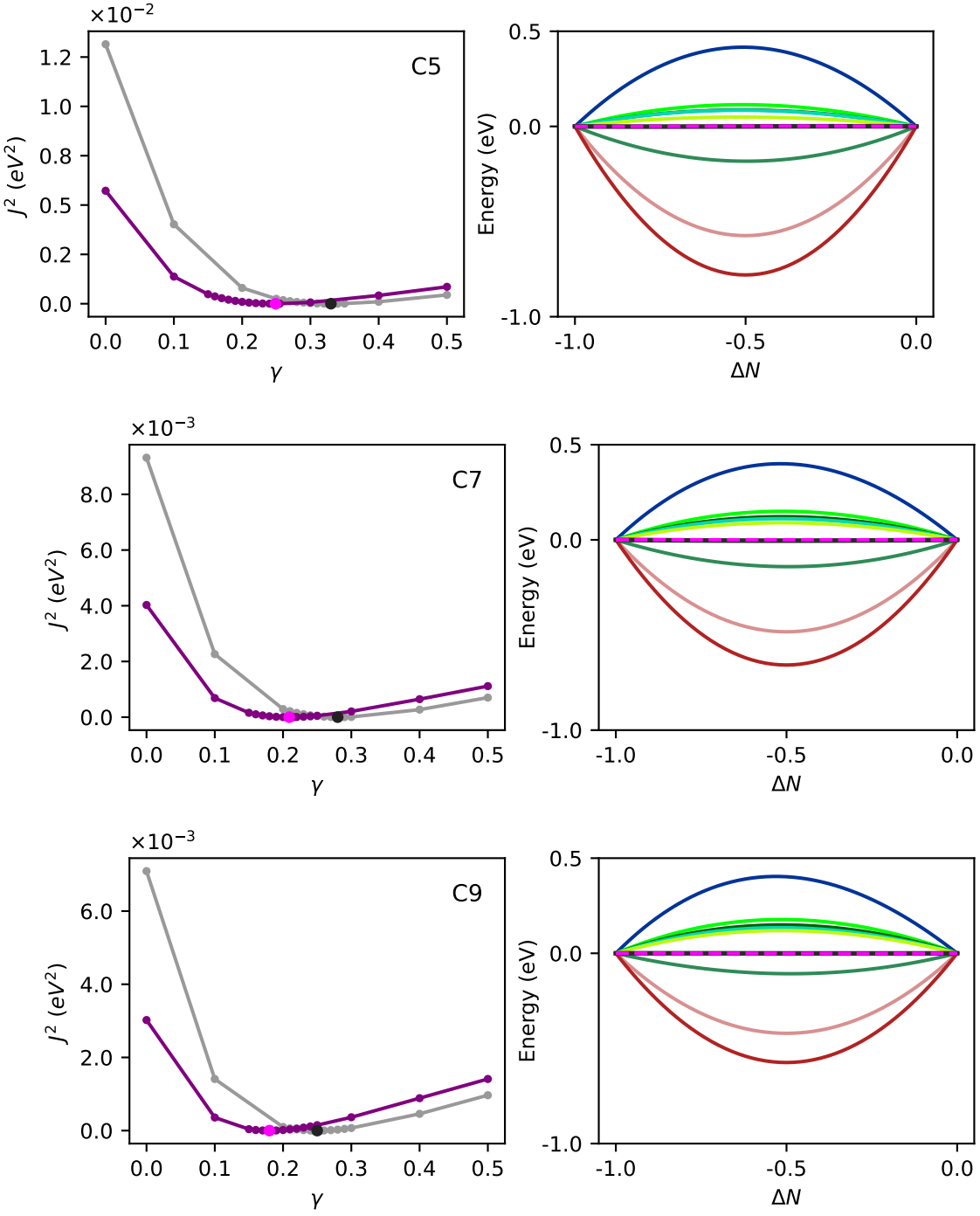
		IP		IP+EA	
	ΔN	$\alpha = 0.00$	0.25	0.00	0.25
C5	$[-1, 0]$	0.00	-0.01	0.00	-0.02
	$[0, +1]$			0.00	0.01
C7	$[-1, 0]$	0.02	0.00	-0.03	-0.02
	$[0, +1]$			-0.02	0.00
C9	$[-1, 0]$	0.00	0.00	-0.01	0.00
	$[0, +1]$			0.00	0.02
M5	$[-1, 0]$	-0.01	-0.00	-0.01	-0.02
	$[0, +1]$			-0.01	0.01
M7	$[-1, 0]$	0.00	0.00	0.00	-0.01
	$[0, +1]$			0.00	0.01
M9	$[-1, 0]$	0.00	0.01	0.00	-0.01
	$[0, +1]$			0.00	0.01
P4	$[-1, 0]$	-0.01	0.04	0.01	0.04
	$[0, +1]$			-0.02	0.03
P6	$[-1, 0]$	-0.01	0.01	0.00	0.01
	$[0, +1]$			-0.01	0.01
P8	$[-1, 0]$	-0.01	-0.02	0.00	-0.02
	$[0, +1]$			-0.01	-0.01
H5	$[-1, 0]$	0.02	0.00	0.02	0.01
	$[0, +1]$			-0.08	-0.05
H6	$[-1, 0]$	0.00	0.02	0.01	0.02
	$[0, +1]$			-0.01	0.02
H8	$[-1, 0]$	-0.01	0.01	0.03	0.01
	$[0, +1]$			-0.04	-0.02
H10	$[-1, 0]$	-0.02	0.00	-0.02	-0.01
	$[0, +1]$			-0.01	0.01

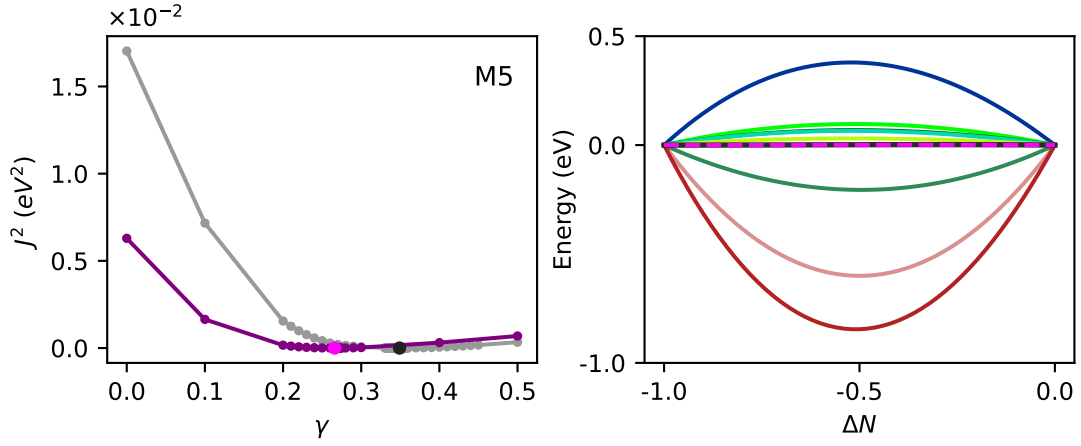
Tab. S4 $\langle S^2 \rangle$ of (N+1) systems (exact: 0.75).

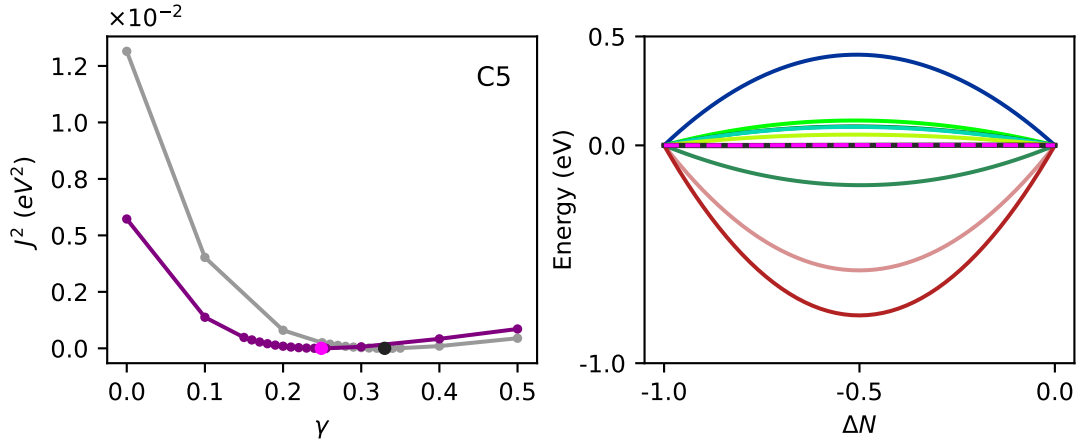
$\langle S^2 \rangle$ N+1	HF	B3LYP	BLYP
C5	0.9445	0.7725	0.7581
C7	1.1532	0.7864	0.7604
C9	1.4135	0.8014	0.7631
M5	0.8843	0.7642	0.7545
M7	0.9964	0.7701	0.7553
M9	1.1425	0.7744	0.7553
P4	0.8314	0.7588	0.7530
P6	0.9311	0.7638	0.7537
P8	1.0730	0.7682	0.7541
H5	0.7548	0.7512	0.7511
H6	0.8372	0.7609	0.7551
H8	0.7541	0.7509	0.7508
H10	0.8372	0.7609	0.7551
H10	0.9069	0.7635	0.7547

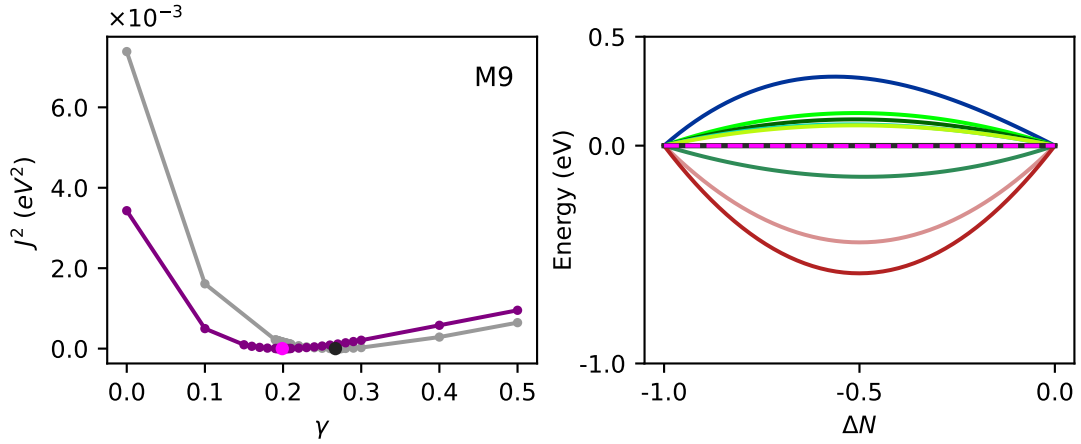
S3 Tuning plots

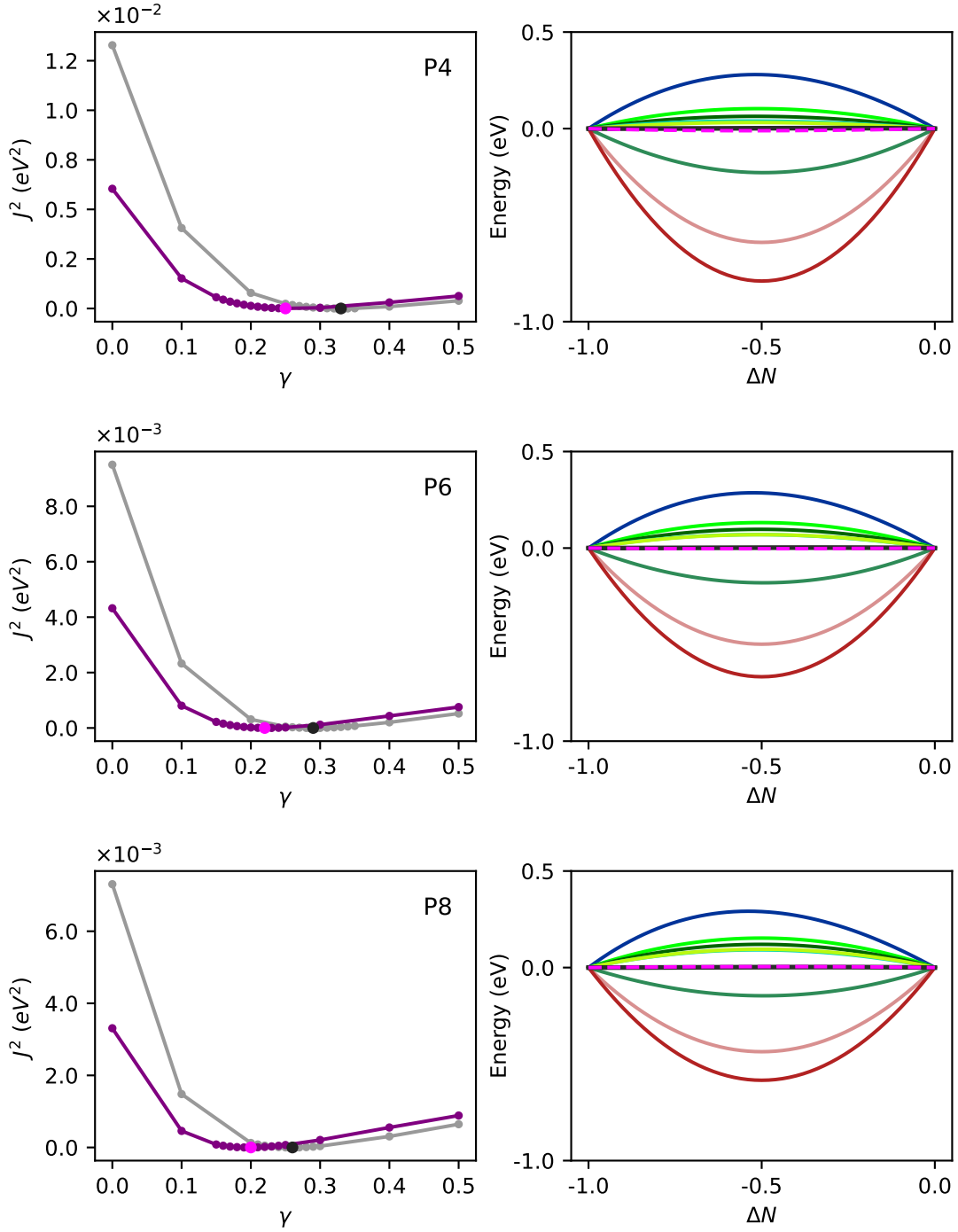
S3.1 IP tuning

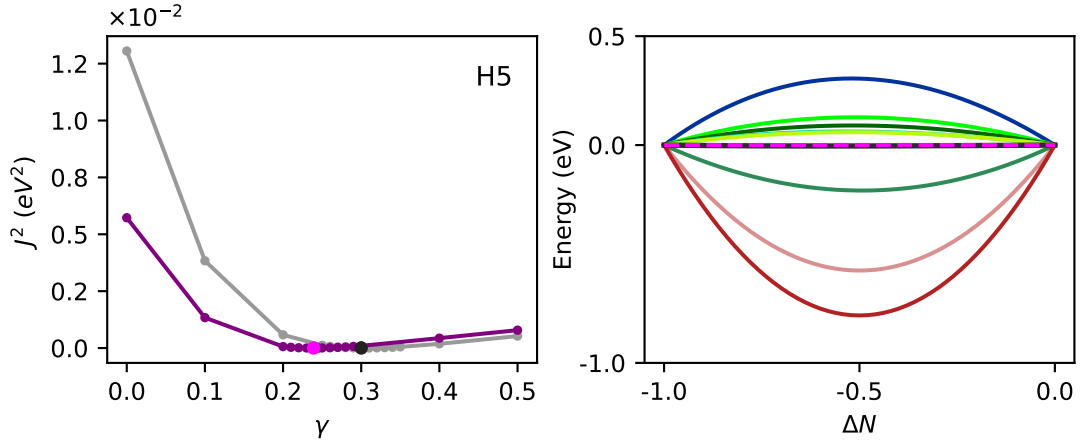


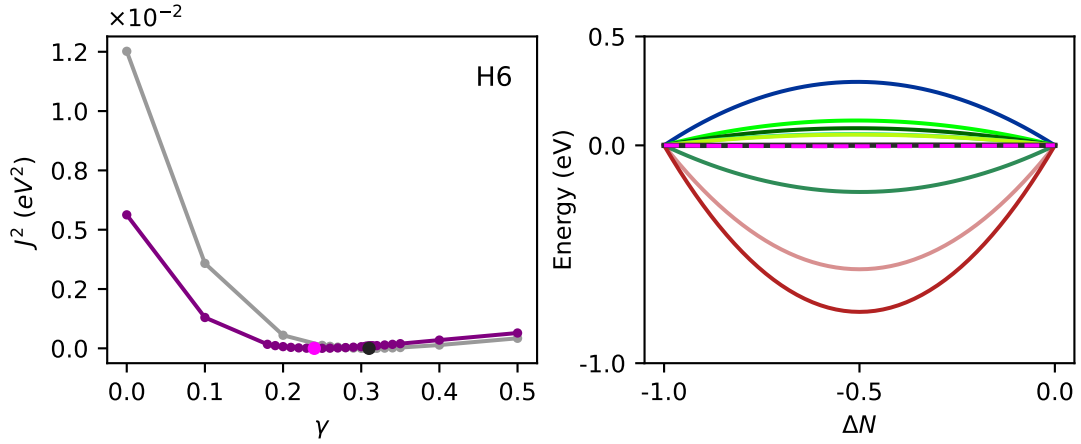

×10⁻²
M5
J² (eV²)
γ
Energy (eV)
ΔN

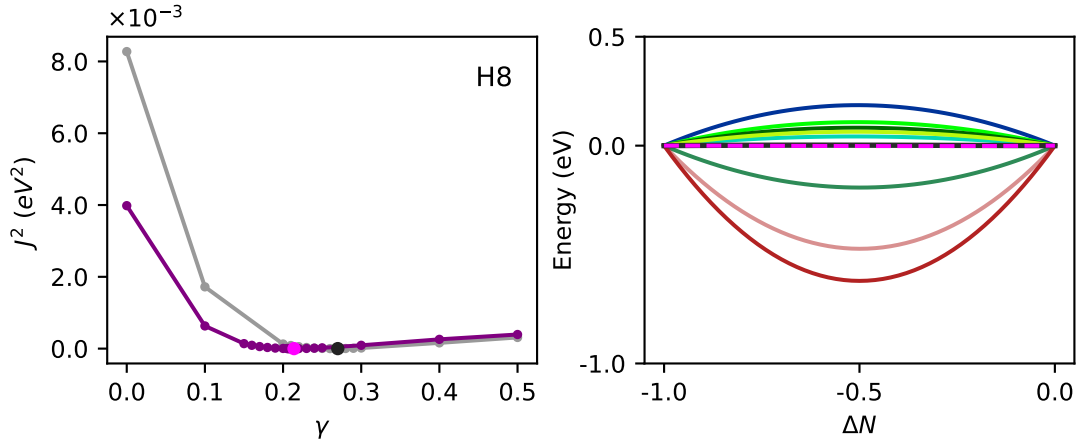

×10⁻²
C5
J² (eV²)
γ
Energy (eV)
ΔN

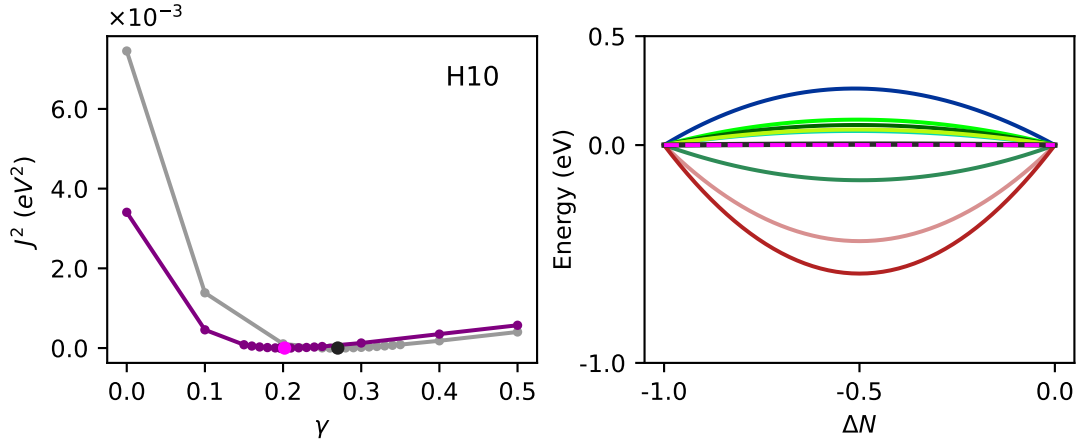

×10⁻³
M9
J² (eV²)
γ
Energy (eV)
ΔN


×10⁻²
P4
J² (eV²)
γ
Energy (eV)
ΔN
×10⁻³
P6
J² (eV²)
γ
Energy (eV)
ΔN
×10⁻³
P8
J² (eV²)
γ
Energy (eV)
ΔN

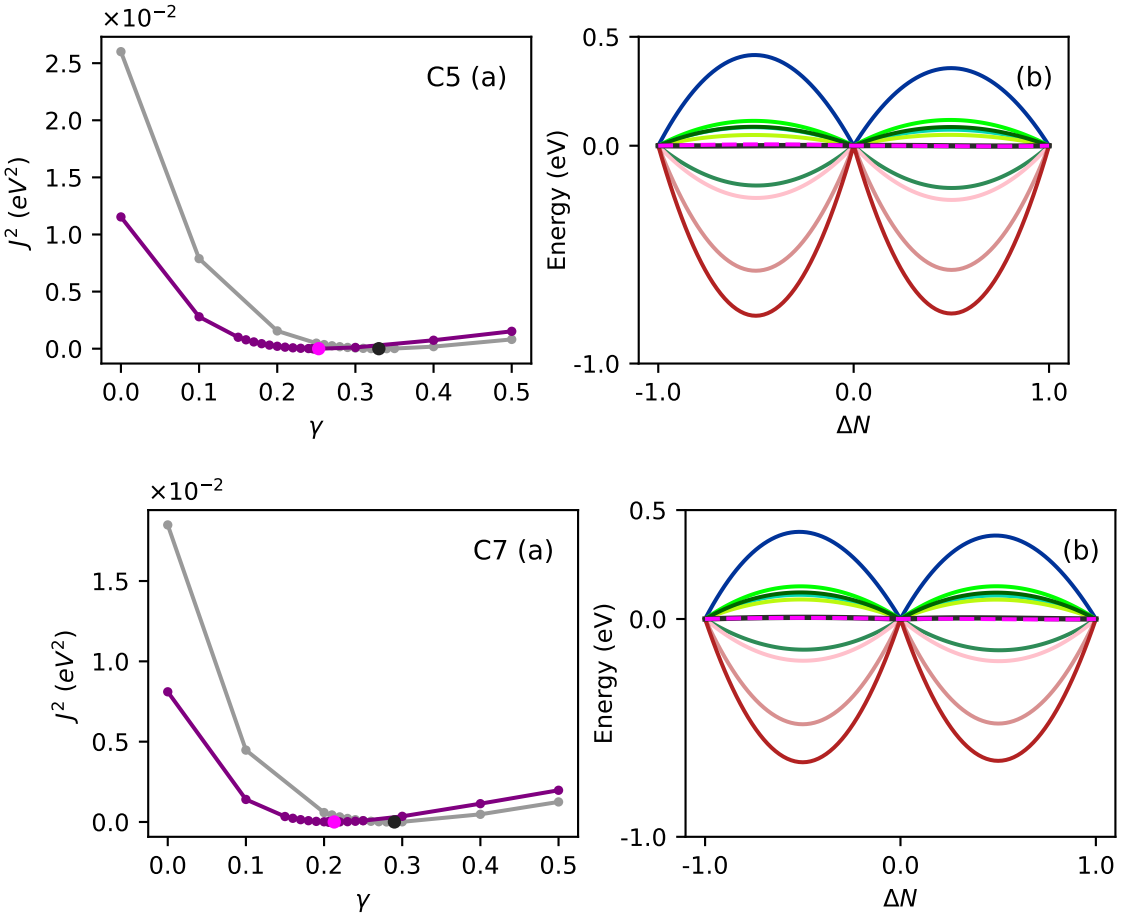

×10⁻²
H5
J² (eV²)
γ
Energy (eV)
ΔN

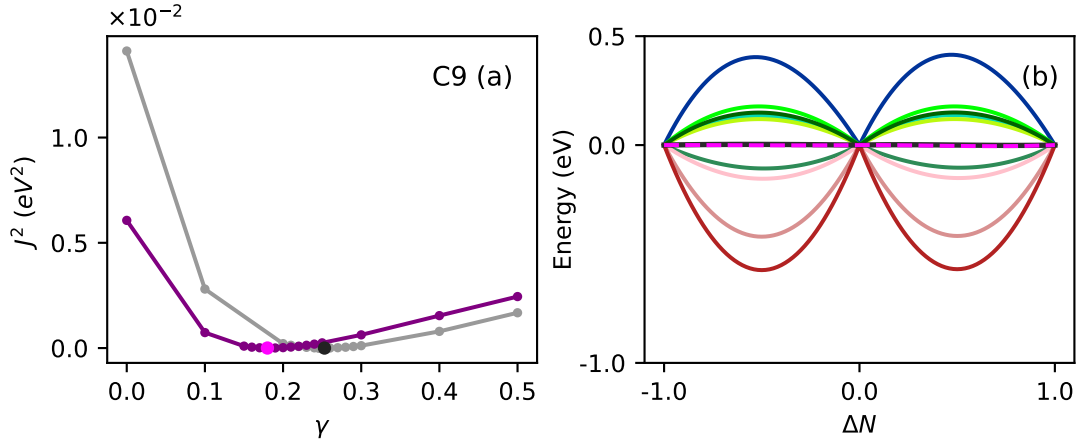

×10⁻²
H6
J² (eV²)
γ
Energy (eV)
ΔN

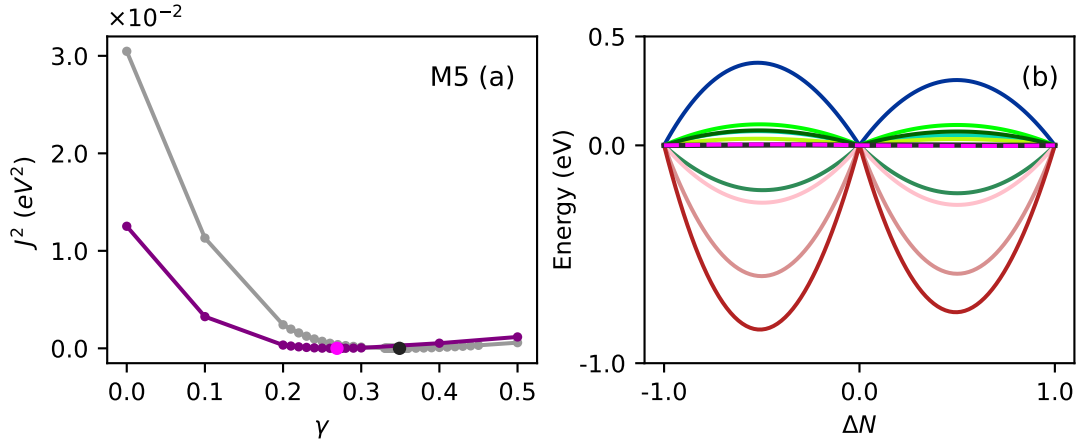

×10⁻³
H8
J² (eV²)
γ
Energy (eV)
ΔN

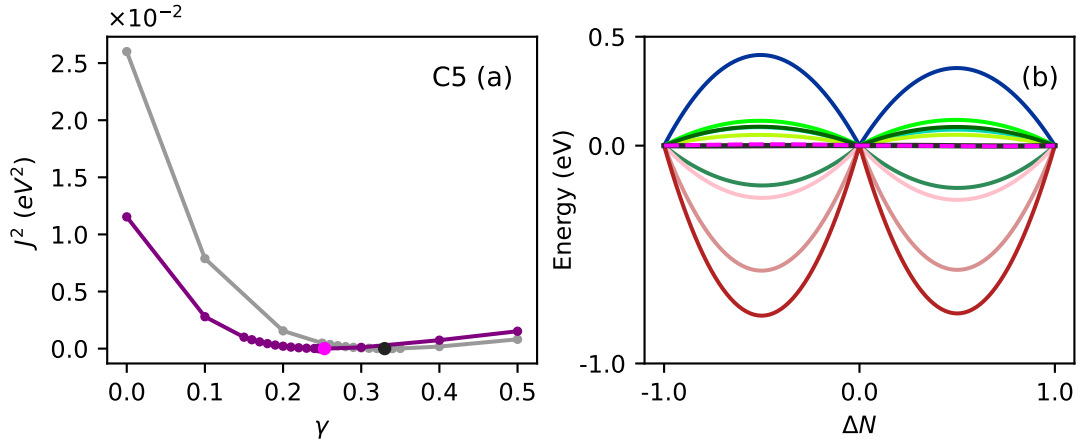


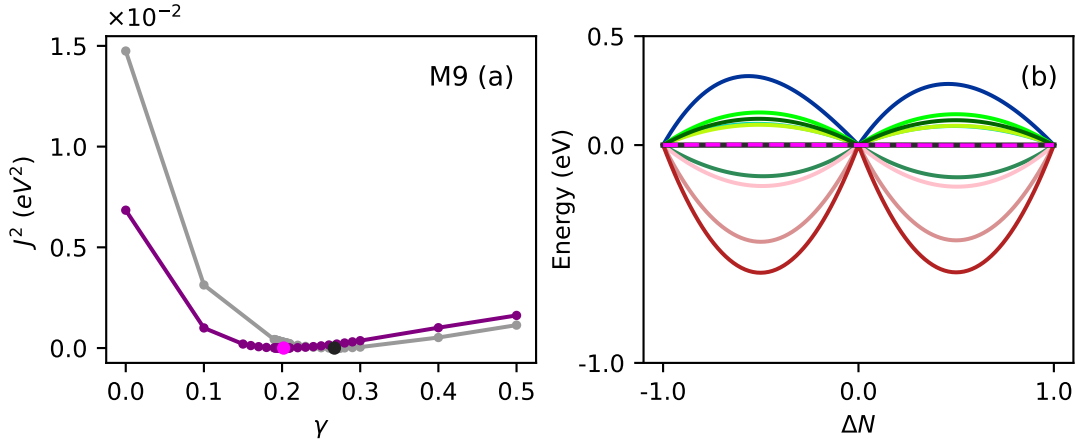
S3.2 IP+EA tuning

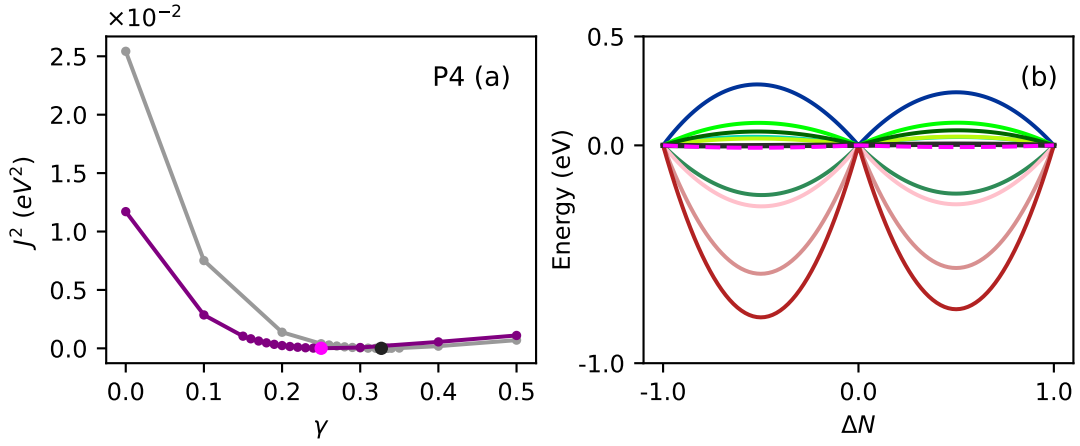


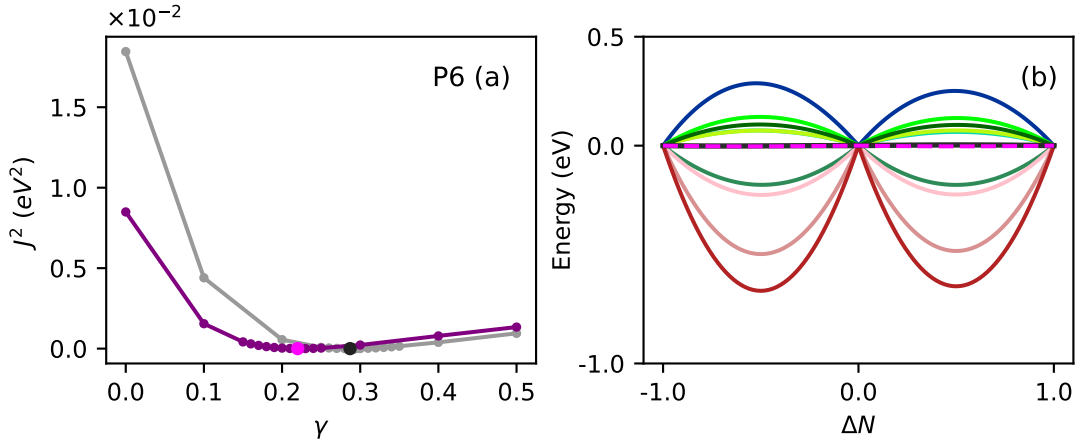

×10⁻²
C9 (a)
J² (eV²)
γ
(b)
Energy (eV)
ΔN


×10⁻²
M5 (a)
J² (eV²)
γ
(b)
Energy (eV)
ΔN


×10⁻²
C5 (a)
J² (eV²)
γ
(b)
Energy (eV)
ΔN


×10⁻²
M9 (a)
J² (eV²)
γ
(b)
Energy (eV)
ΔN


×10⁻²
P4 (a)
J² (eV²)
γ
(b)
Energy (eV)
ΔN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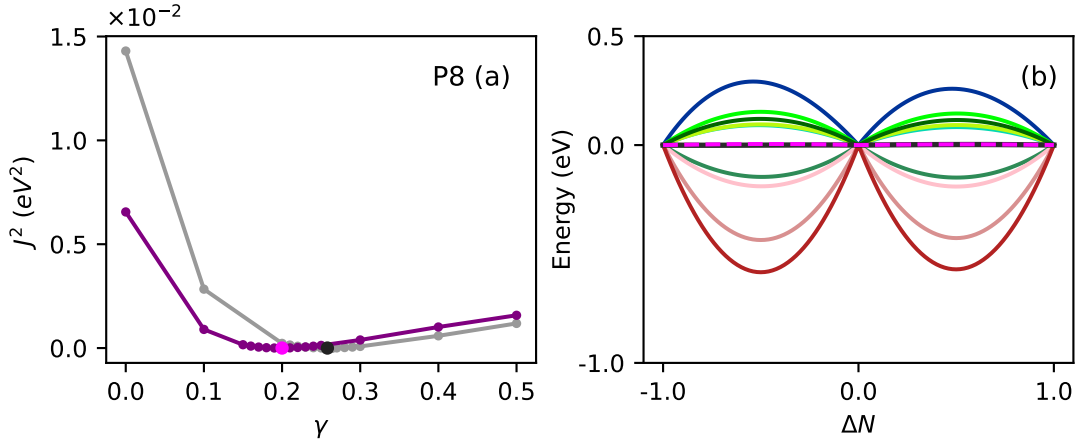
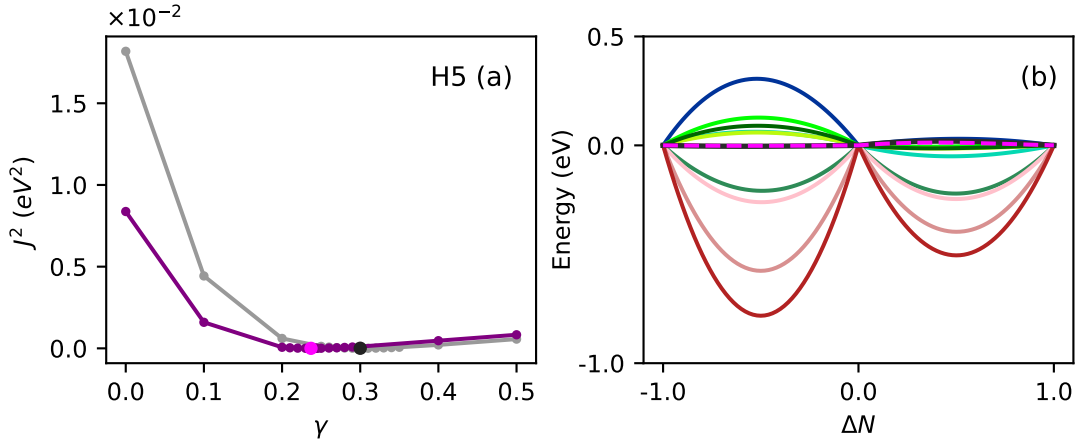
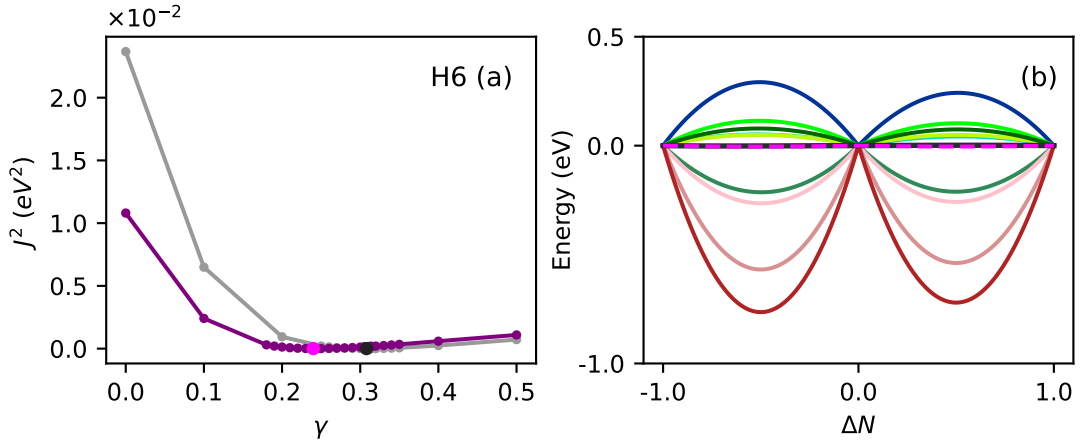
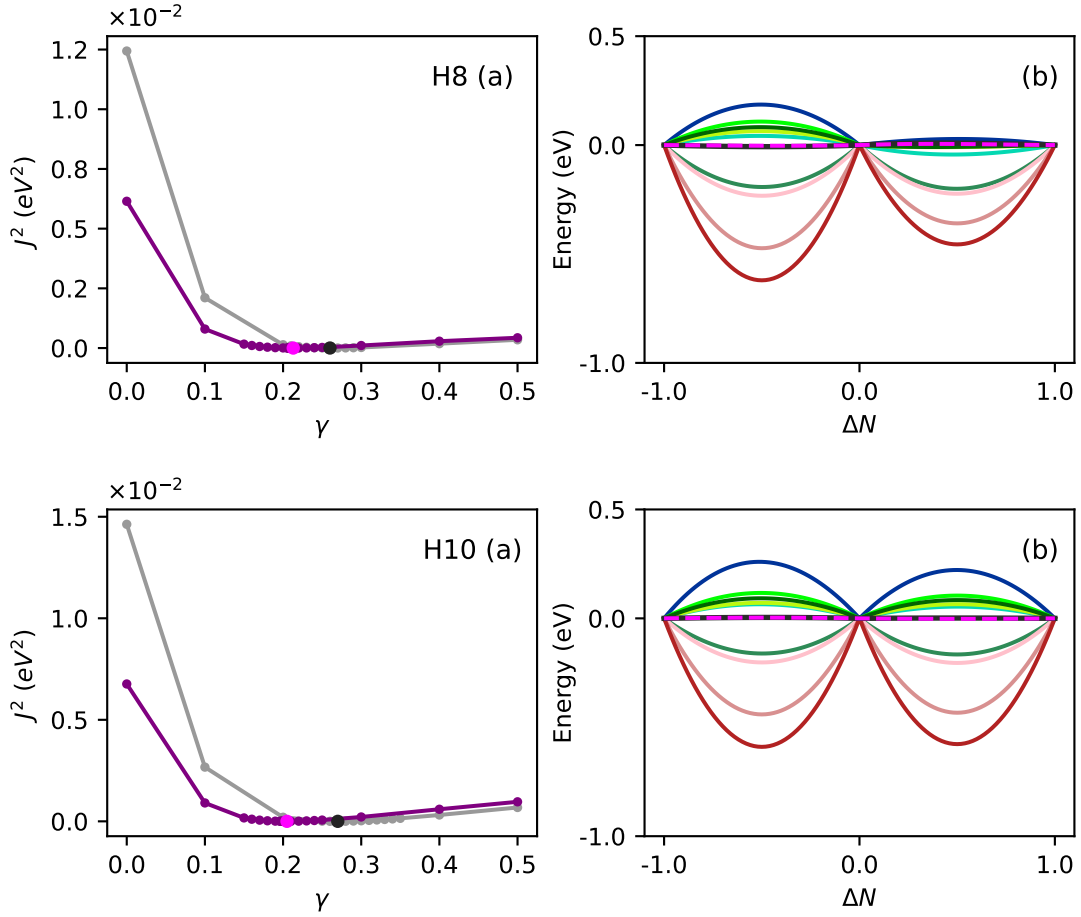
P6 (a)
J² (eV²)
γ
(b)
Energy (eV)
ΔN


×10⁻²
P8 (a)
J² (eV²)
γ
(b)
Energy (eV)
ΔN


×10⁻²
H5 (a)
J² (eV²)
γ
(b)
Energy (eV)
ΔN


×10⁻²
H6 (a)
J² (eV²)
γ
(b)
Energy (eV)
ΔN


×10⁻²
H8 (a)
J² (eV²)
γ
(b)
Energy (eV)
ΔN
H10 (a)

S4 Stability Calculations

Tab. S5 Hartree-Fock stability calculation.

		S=0			S=1
Molecule	ΔE_{ST} [a]	RHF	UHF	ΔE_{bs} [b]	UHF
M5	1.1596	✓	✓	0	✓
M7	-1.9405	×	×	-0.10	✓
M9	-2.4344	×	×	-0.34	✓
O_2	-5.6047	×	×	-1.54	✓
O_3	-5.0297	×	×	-1.97	×
Pentacence	-2.9952	×	×	-2.70	×

[a] ΔE_{ST} (eV) is determined by TDHF without Tamm-Dancoff approximation.
[b] $\Delta E_{bs} = E_{bsUHF} - E_{UHF}$ (eV) Broken-symmetry (bs) energy is obtained by keyword guess=(mix,INDO)

Tab. S6 B3LYP stability calculation.

		S=0			S=1
Molecule	ΔE_{ST} [a]	RB3LYP	UB3LYP	ΔE_{bs} [b]	UB3LYP
M5	3.1901	✓	✓	0	✓
M7	2.2614	✓	✓	0	✓
M9	1.7465	✓	✓	0	✓
O_2	-1.6225	×	×	-1.26	✓
O_3	-1.2743	×	×	-0.02	✓
Pentacence	-0.3733	×	×	-0.01	✓

[a] ΔE_{ST} (eV) is determined by TDDFT (B3LYP) without Tamm-Dancoff approximation.
[b] $\Delta E_{bs} = E_{bsB3LYP} - E_{B3LYP}$ (eV) Broken-symmetry (bs) energy is obtained by keyword guess=(mix,INDO)