

Supporting Information for

**Understanding Plasmon Coupling in Nanoparticle Dimers using
Molecular Orbitals and Configuration Interaction**

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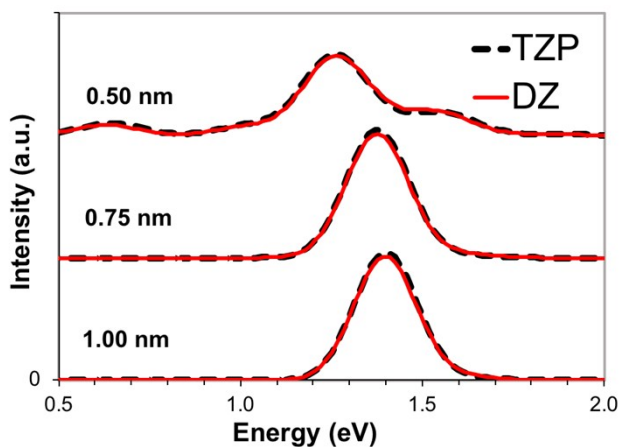


Figure S1. Comparison of calculated spectra for Ag_8 atomic wire dimers at various distances using the PBE/TZP (black-dashed lines) and PBE/DZ (red-solid lines) levels of theory.

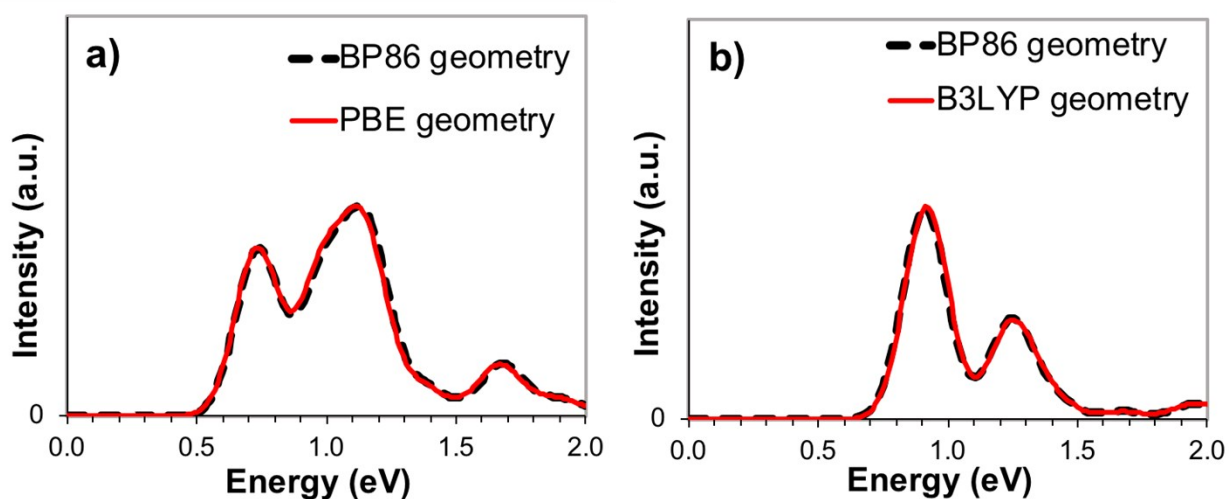


Figure S2. Comparison of calculated spectra for Ag_8 atomic wire dimers at 0.4 nm separation. a) TDDFT is performed with PBE/DZ level for both cases. Black-dashed line shows the spectrum where the Ag_8 geometry is obtained at the BP86/DZ level of theory whereas the red-solid line shows the spectrum where the Ag_8 geometry is obtained at the PBE/DZ level of theory. b) TDDFT is performed with B3LYP/DZ level for both cases. Black-dashed line shows the spectrum where the Ag_8 geometry is obtained at the BP86/DZ level of theory whereas the red-solid line shows the spectrum where the Ag_8 geometry is obtained at the B3LYP/DZ level of theory.

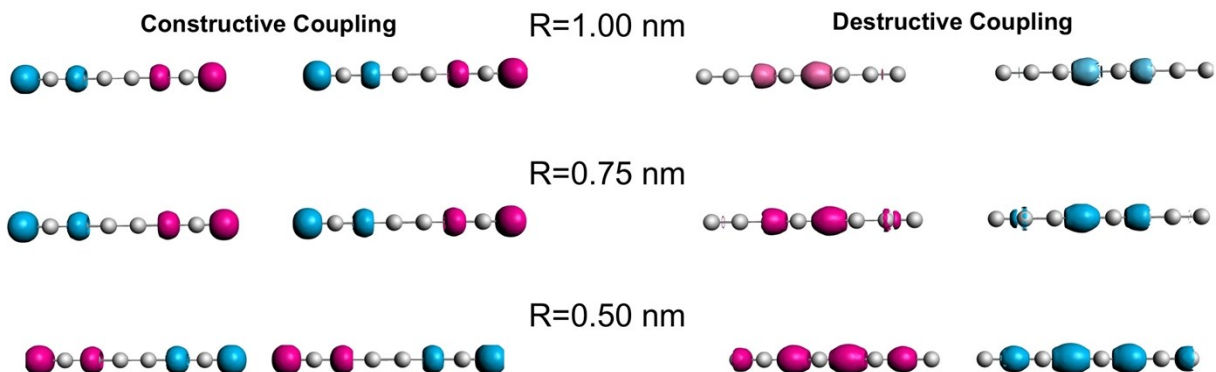


Figure S3. Calculated TFDs for the constructive and destructive coupling of $4^a\Sigma_u \rightarrow 5^b\Sigma_g$ and $4^b\Sigma_g \rightarrow 5^a\Sigma_u$ configurations at 1.00, 0.75 and 0.50 nm gap distances. The energies, intensities and weights of each configuration are given in Table S1.

Table S1. Calculated Energies, Intensities, and Important Configurations with Weights and Dipole Moment Contributions for the Constructive and Destructive Coupling of $4^a\Sigma_u \rightarrow 5^b\Sigma_g$ and $4^b\Sigma_g \rightarrow 5^a\Sigma_u$ Configurations at 1.00, 0.75 and 0.50 nm Gap Distances Calculated at the PBE/DZ Level of Theory					
Excited State #	Energy (eV)	Oscillator Strength (a.u.)	Transitions	Weight	Contribution to Transition Dipole Moment
1.00 nm Gap Distance					
1	0.60	0.00	$4^a\Sigma_u \rightarrow 5^b\Sigma_g$	0.50	9.08
			$4^b\Sigma_g \rightarrow 5^a\Sigma_u$	0.50	-9.05
2	1.40	4.21	$4^b\Sigma_g \rightarrow 5^a\Sigma_u$	0.48	5.77
			$4^a\Sigma_u \rightarrow 5^b\Sigma_g$	0.48	5.78
0.75 nm Gap Distance					
1	0.60	0.00	$4^a\Sigma_u \rightarrow 5^b\Sigma_g$	0.51	9.31
			$4^b\Sigma_g \rightarrow 5^a\Sigma_u$	0.49	-8.84
2	1.37	4.21	$4^b\Sigma_g \rightarrow 5^a\Sigma_u$	0.47	5.70
			$4^a\Sigma_u \rightarrow 5^b\Sigma_g$	0.45	5.75
0.50 nm Gap Distance					
1	0.63	0.36	$4^a\Sigma_u \rightarrow 5^b\Sigma_g$	0.60	11.28
			$4^b\Sigma_g \rightarrow 5^a\Sigma_u$	0.38	-6.36
2	1.24	2.13	$4^b\Sigma_g \rightarrow 5^a\Sigma_u$	0.30	-4.00
			$4^a\Sigma_u \rightarrow 5^b\Sigma_g$	0.19	-4.53

Calculation of off-diagonal coupling elements using TDA

Within the TDA formalism, the secular equation for the excited state energies reads:

$$\mathbf{A}\mathbf{X} = \omega\mathbf{X} \quad (\text{S1})$$

where \mathbf{A} is the Hamiltonian for the singly excited determinants in matrix form, \mathbf{X} is the matrix for expansion coefficients for singly excited determinants, and ω collects the excited state energies. If one only considers two singly excited determinants among the possible singly excited determinants, such as $4^a\Sigma_u \rightarrow 5^b\Sigma_g$ and $4^b\Sigma_g \rightarrow 5^a\Sigma_u$ in the case of Ag_8 dimers, the TDA equation reduces to the Hamiltonian shown in Eq. 1. We note that this would not be the case for the full TDDFT method due to the \mathbf{B} matrix in the formalism. With TDA, the matrix elements for the Hamiltonian in Eq. 1 are given as:

$$H_{ia,jb} = \delta_{ij}\delta_{ab}\Delta_{ia} + (ia|jb) - c_{HF}(ij|ab) + (1 - c_{HF})(ia|f_{XC}|jb) \quad (\text{S2})$$

Here, indices ia and jb corresponds to singly excited $4^a\Sigma_u \rightarrow 5^b\Sigma_g$ and $4^b\Sigma_g \rightarrow 5^a\Sigma_u$ determinants, Δ denotes the orbital energy difference, c_{HF} denotes the amount of HFX and f_{XC} shows the kernel of the exchange-correlation functional in DFT. From this equation, it is clear how the amount of HFX (c_{HF}) alters the coupling between two configurations.

If we reduce our occupied-virtual orbital space to $4^a\Sigma_u$ (occupied), $4^b\Sigma_g$ (occupied), $5^b\Sigma_g$ (virtual), and $5^a\Sigma_u$ (virtual) for Ag_8 dimers, the TDA calculation will result in two optically-allowed excited states. At long distances, the relationship between the energies of these excited states and matrix elements of Eq. S2 is given in Eq. 2 and 3. Using the result of the TDA calculation and these relations, one can obtain the values of on-diagonal (α) and off-diagonal (β) terms. One can also obtain α directly using only one configuration instead of two in a modified-TDA calculation. In Table S2, we summarize these results for the functionals employed in this work.

Table S2. Calculated On-diagonal (α) and Off-diagonal (β) Terms.

Functional	$\alpha - \beta$ (eV)	$\alpha + \beta$ (eV)	$\alpha^{(a)}$ (eV)	$\beta^{(a)}$ (eV)	$\alpha^{(b)}$ (eV)	$\alpha^{(c)}$ (eV)
BLYP	0.56	2.23	1.40	0.84	1.39	1.42
B3LYP-10%	0.76	2.09	1.43	0.67	1.42	1.44
B3LYP-20%	0.99	1.97	1.48	0.49	1.47	1.49
B3LYP-30%	1.23	1.87	1.55	0.32	1.54	1.56
B3LYP-40%	1.49	1.80	1.65	0.15	1.64	1.66
B3LYP-50%	1.78	1.75	1.77	-0.02	1.76	1.78
B3LYP-60%	1.71	2.04	1.88	-0.17	1.87	1.89
Hartree-Fock	3.35	1.78	2.56	-0.79	2.55	2.58

(a) α and β are calculated from the $\alpha - \beta$ and $\alpha + \beta$ values.

(b) α is calculated directly from the $4^a\Sigma_u \rightarrow 5^b\Sigma_g$ transition by reducing the occupied-virtual orbital space to only $4^a\Sigma_u$ and $5^b\Sigma_g$ in the TDA calculation.

(c) α is calculated directly from the $4^b\Sigma_g \rightarrow 5^a\Sigma_u$ transition by reducing the occupied-virtual orbital space to only $4^b\Sigma_g$ and $5^a\Sigma_u$ in the TDA calculation.

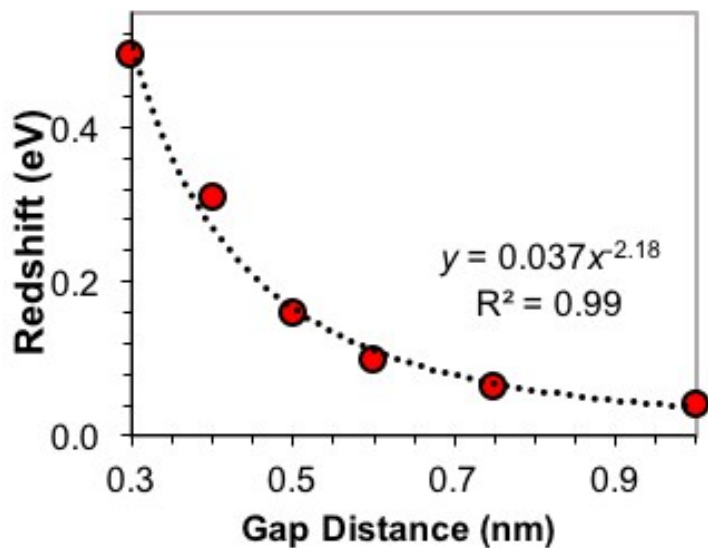


Figure S4. The distance dependence of the redshift for the longitudinal peak in Ag_8 dimers calculated with B3LYP-60% and TDDFT. The dotted line shows the best-fit line for the data.

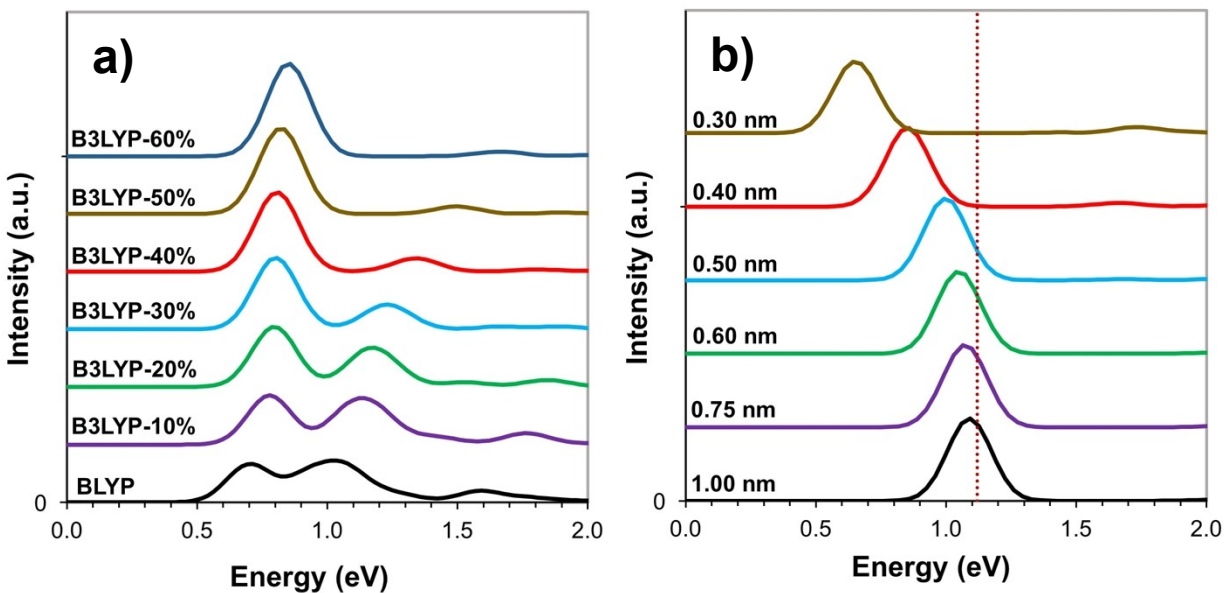


Figure S5. Calculated spectra for Ag_8 atomic wire dimers using hybrid functionals and sTDDFT formalism. In a) we show the spectra at 0.40 gap distances with different functionals of varying HFX. In b) we show the gap distance dependence of calculated spectra for Ag_8 atomic wire dimers with the B3LYP-60% functional, similar to Figure 8 in the main text.