The electron delocalization range in atoms and on molecular surfaces

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Supporting Information

SI-I. SUPPLEMENTARY FIGURES AND TABLES

TABLE SI-1: Lithium atom in various basis sets. Kinetic energy per electron KE/e (Hartree), atom-averaged delocalization D_A (bohr), radius r_{surf} of the 0.001 electrons/bohr^{-3} density isosurface (bohr), and LOL(r_{surf}) (unitless) & surface delocalization $D(r_{surf})$ (bohr).

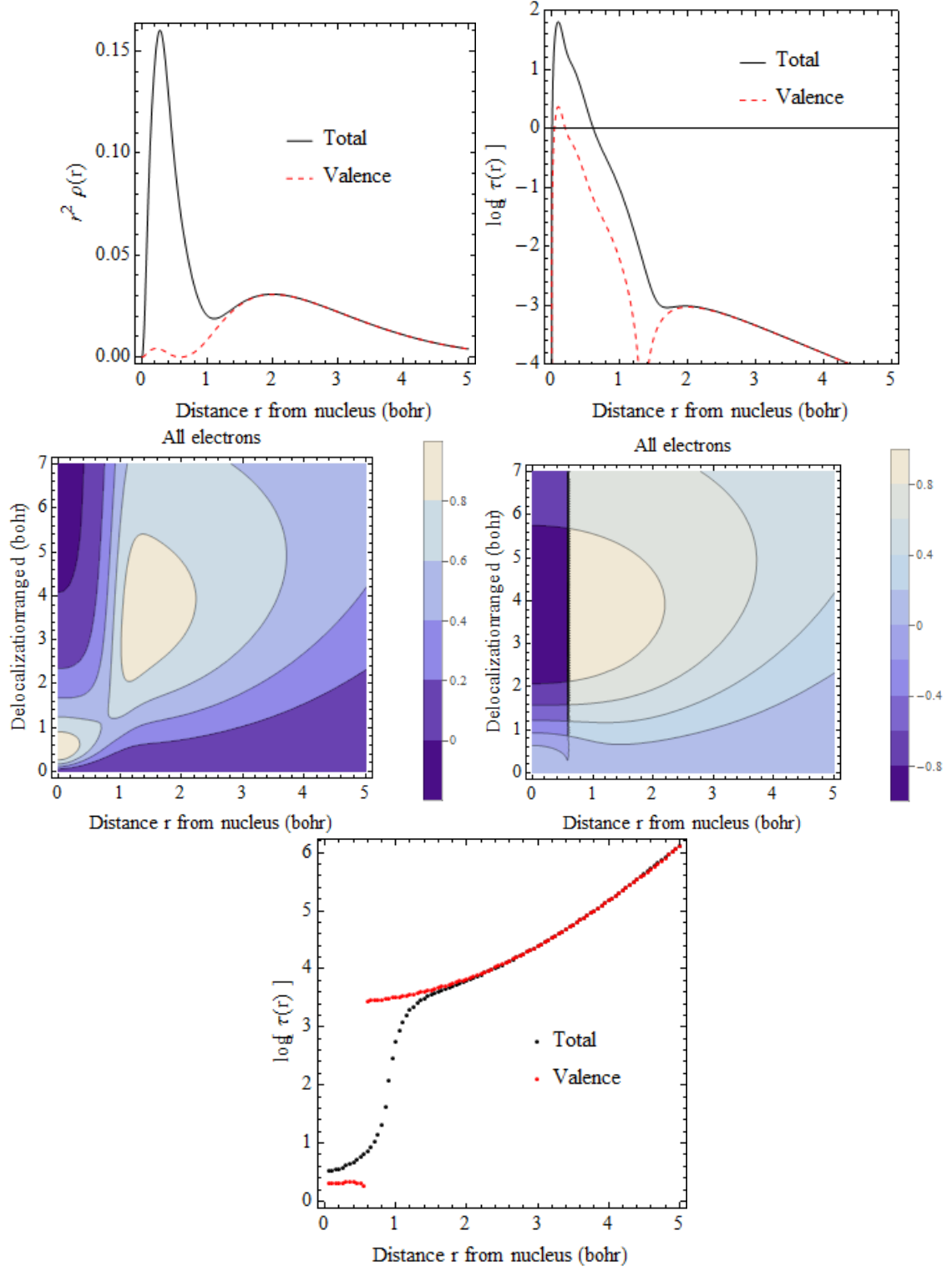| Basis	KE/e	D_A	r_{surf}	10^2 LOL(r_{surf})	$D(r_{surf})$
STO-3G	2.476	3.0692	3.966	2.301	5.606
3-21G	2.457	3.1011	4.062	3.336	6.410
6-31G	2.484	3.1010	4.182	3.305	6.163
6-31+G(d)	2.485	3.1021	4.159	3.227	6.309
6-311+G(2d)	2.477	3.1046	4.178	3.463	6.346
cc-pVTZ	2.478	3.1055	4.173	3.312	6.320
aug-cc-pVQZ	2.478	3.1054	4.169	3.337	6.334

FIG. SI-1: Valence and all-electron calculations on isolated spherical Be atom, in the uncontracted 3-21G basis set. (Top left) $r^2\rho(r)$. (Top right) Kinetic energy density $\tau(r)$, log scale. (Middle) Contour plots of $\text{EDR}(r,d)$ for (left) all and (right) valence electrons. The EDR is negative near the nucleus due to core-valence orthogonality, which makes $\gamma(\vec{r}, \vec{r}\,') < 0$ when points $\vec{r}$ and $\vec{r}\,'$ are in core and valence regions. (Bottom) $D(r)$.
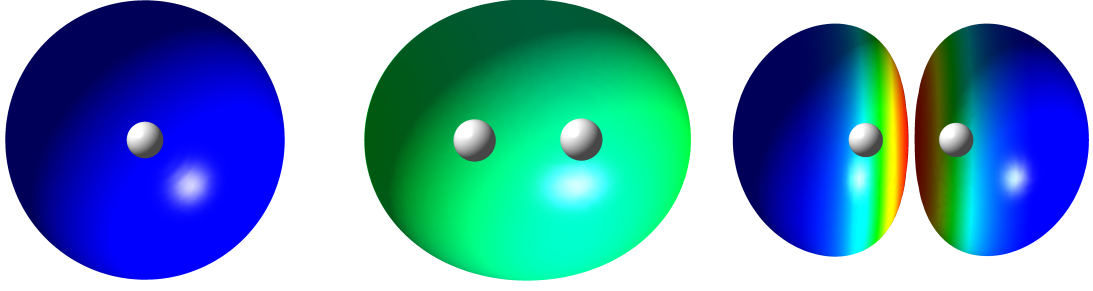
FIG. SI-2: Density isosurfaces from Figure 1, painted with the localized orbital locator $\text{LOL}(\vec{r})$ from 0 (red) to 0.08 (blue). The LOL is near zero in this low-density region.
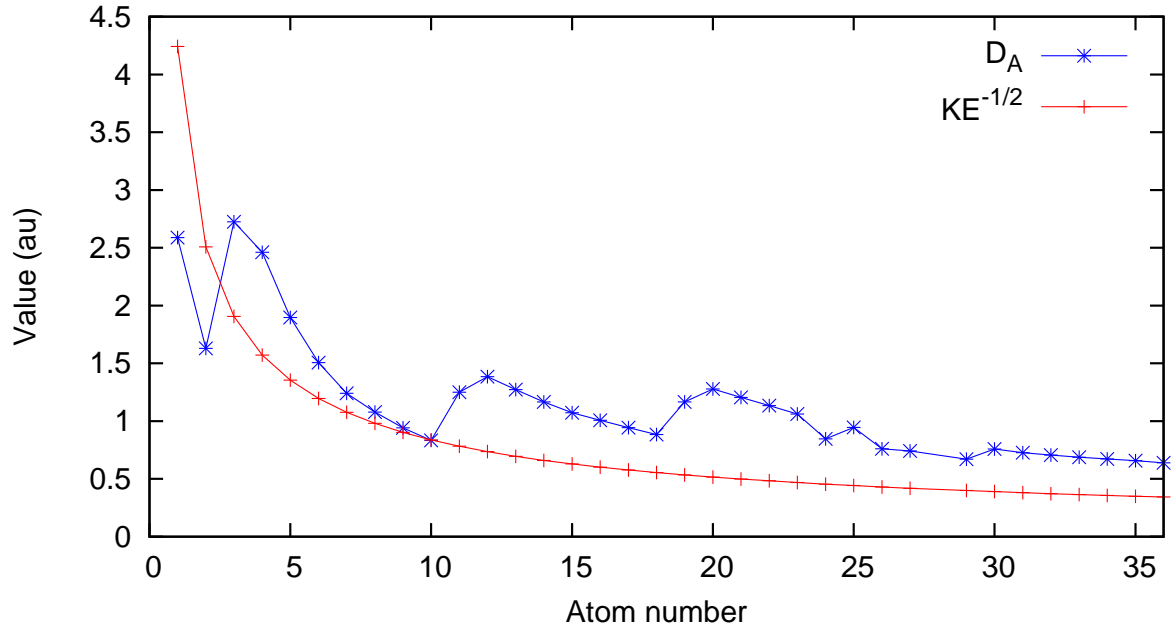

FIG. SI-3: Atomic delocalization lengths and $\text{KE}^{-1/2}$ for the atoms in Figure 2, evaluated using full rather than valence density matrices.
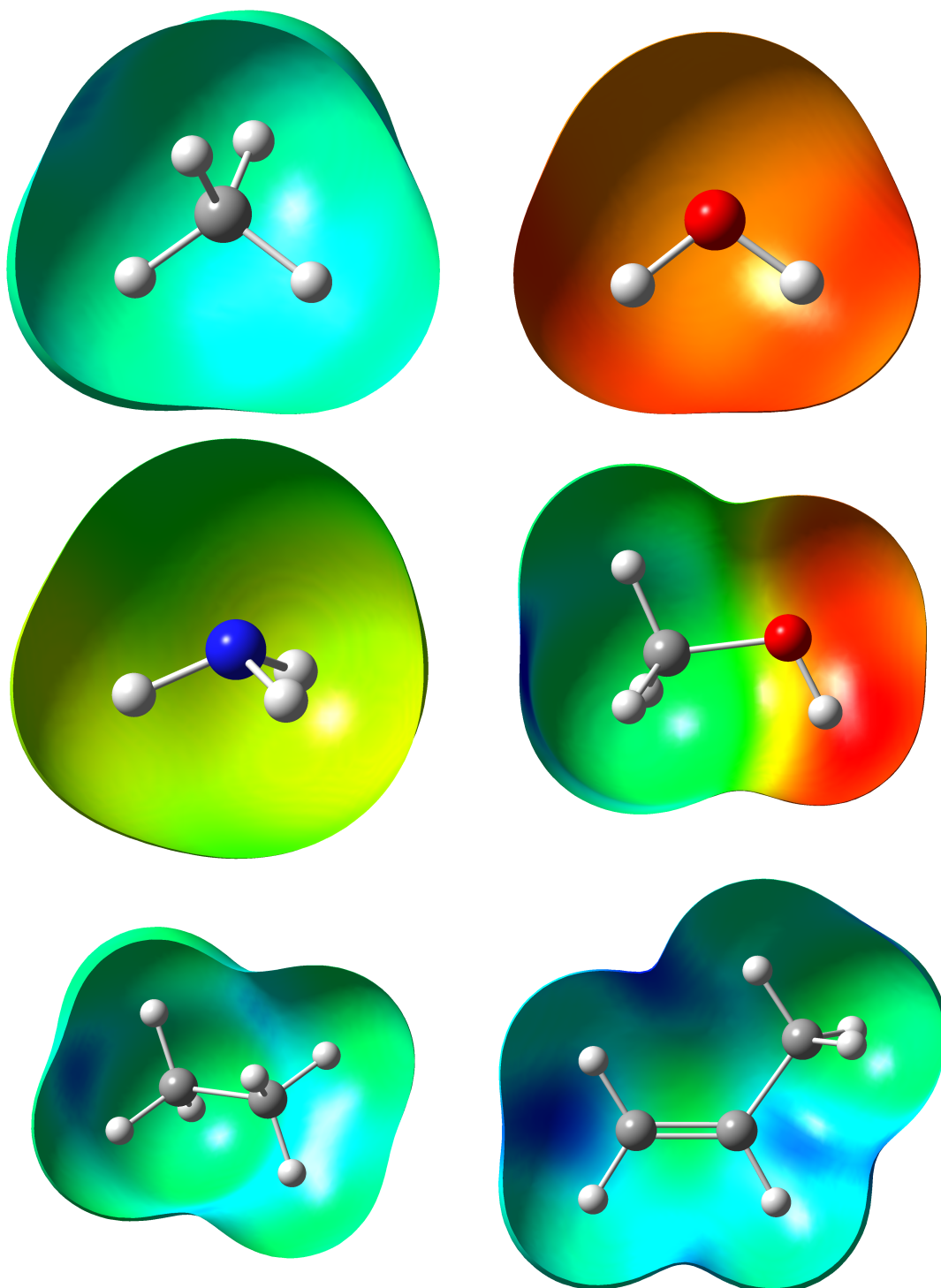
FIG. SI-4: Surface delocalization from B3LYP/6-31+G(d,p) calculations on small molecules. Reading left to right from top left : CH_4, H_2O, NH_3, CH_3OH, C_2H_6, C_3H_6. $D(\vec{r})$ plotted from 2.5 bohr (red) to 3.2 bohr (blue).
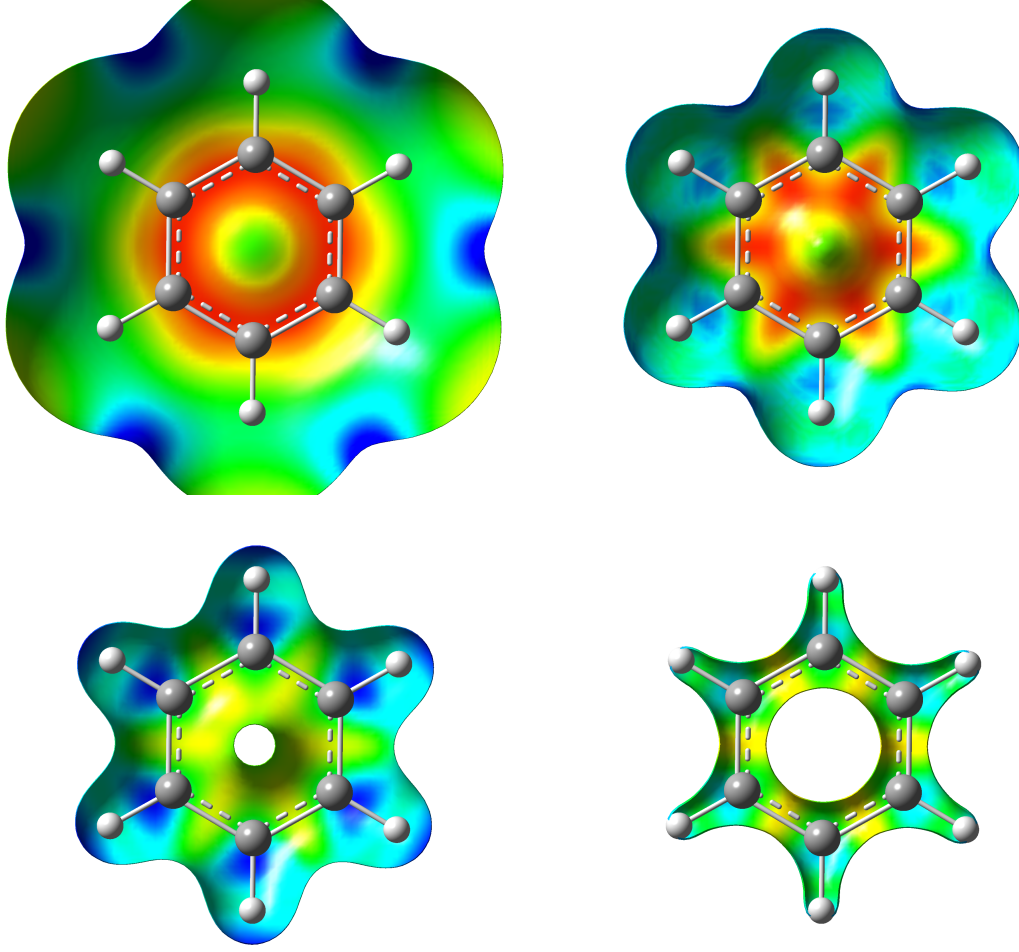
FIG. SI-5: Surface delocalization of Figure 5 plotted on different density isosurfaces. Top left: $\rho = 0.0002$ bohr^{-3}, $D(\vec{r})$ from 3.4 bohr (red) to 3.7 bohr (blue). Top right: $\rho = 0.005$ bohr^{-3}, $D(\vec{r})$ from 2.3 bohr (red) to 2.5 bohr (blue). Bottom left: $\rho = 0.02$ bohr^{-3}, $D(\vec{r})$ from 1.8 bohr (red) to 2.1 bohr (blue). Bottom right: $\rho = 0.1$ bohr^{-3}, $D(\vec{r})$ from 1.3 bohr (red) to 1.8 bohr (blue).
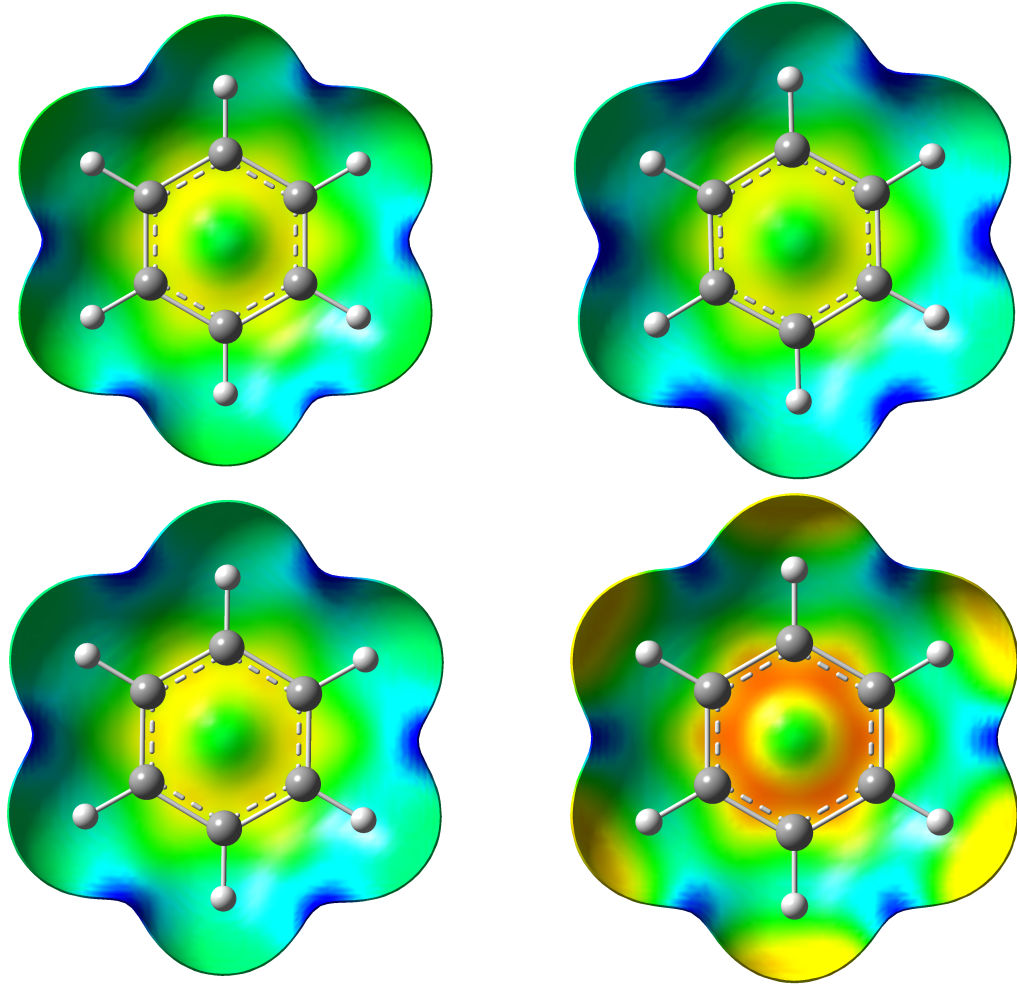
FIG. SI-6: Benzene surface delocalization of Figure 5, plotted on the $\rho(\vec{r}) = 0.001$ electrons/bohr^3 density isosurface for different density matrices. $D(\vec{r})$ from 2.8 bohr (red) to 3.1 bohr (blue). Top left: Hartree-Fock/6-311++G(2d,2p). Top right: LDA/6-311++G(2d,2p). Bottom left: B3LYP/6-311++G(2d,2p). Bottom right: Hartree-Fock/3-21G. Qualitative trends all match Figure 5.
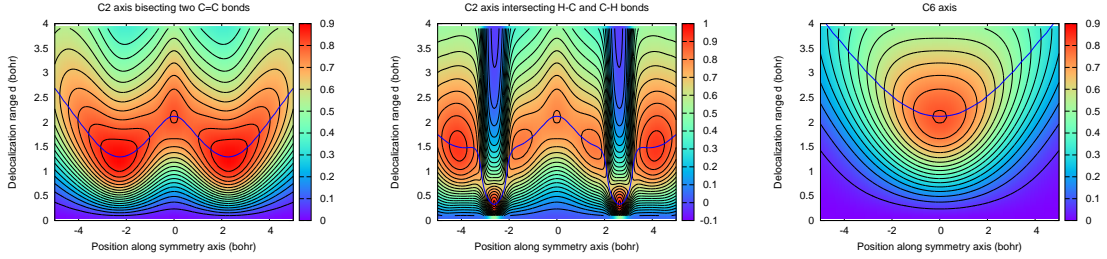
FIG. SI-7: Surface and contour plots of $EDR(x; d)$ for points x along three of benzene's symmetry axes. Abscissa denotes position x, ordinate denotes length scale d, and surfaces are shaded from small/negative EDR in blue to EDR approaching 1 in red. Thick blue lines denote $D(x)$ obtained from Eq. 4. Calculations use the geometry and CCSD density matrices of Figure 5. $EDR(x; d)$ has a single maximum in d at each point x. $D(x)$ is relatively long outside of the C=C bonds (i.e., between adjacent C-H bonds).

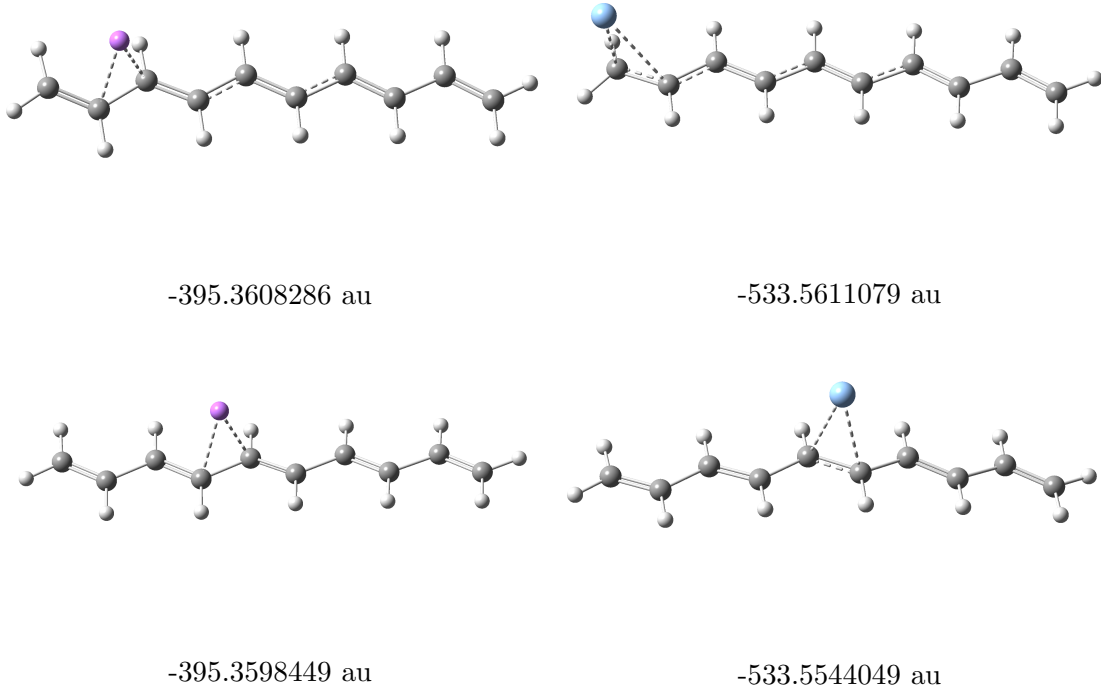-395.3608286 au   -533.5611079 au

-395.3598449 au   -533.5544049 au

FIG. SI-8: ωB97X-D/LANL2DZ geometries and total energies (au) for hard Li$^+$ (left) and soft Ag$^+$ (right) binding to 1,3,5,7,9-pentadecene. Soft Ag$^+$ exhibits a greater prefernce for the larger surface delocalization of the terminal C=C bond (Figure 4), while hard Li$^+$ has comparable preferences for both C-C bonds.
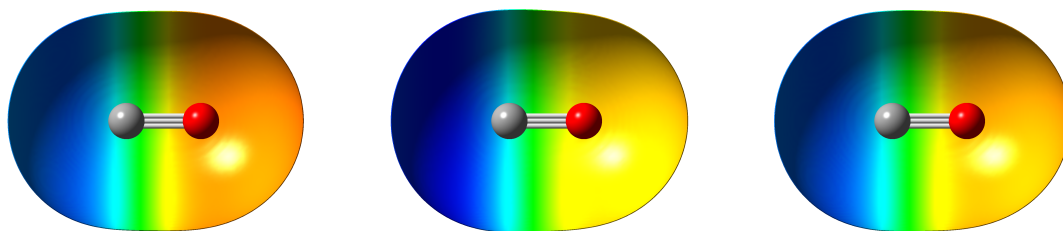
FIG. SI-9: Surface delocalization of carbon monoxide at equilibrium geometry. HF (left), LDA (middle), and CCSD (right) calculations, details as in Figure 6.

SI-II.   DELOCALIZATION AND KINETIC ENERGY FOR DIFFUSE DENSITIES

Here we show how an atom's kinetic energy and atomic delocalization vary as part of the density becomes delocalized. We consider a single electron shared between a tight and diffuse s-type Gaussian basis function,

$$\psi(\vec{r}) \;=\; C_a \left(\chi_{a=1}(\vec{r}) + \lambda \chi_a(\vec{r}) \right) \tag{SI-1}$$

$$\chi_a(\vec{r}) \;=\; \left(\frac{2}{\pi a^2} \right)^{3/4} \exp\left(-\frac{|\vec{r}|^2}{a^2} \right) \tag{SI-2}$$

The diffuse basis function spans distance a (bohr), while the tight function has $a = 1$ bohr. Parameter λ gives the fraction of electron density in the diffuse orbital. Figure SI-10 shows the spherically symmetric electron density at three values of a (at $\lambda = 1$), illustrating how large a partitions the density into tight and diffuse regions. Figure SI-11 shows contour plots of $\mathrm{EDR}(r; d)$ at the same three a values. At large a, $\mathrm{EDR}(r; d)$ has two local maxima in d for points r near the nucleus: a maximum at small d from the localized electrons, and a maximum at large d from the delocalized electrons. The characteristic delocalization length $D(r)$ exhibits a discontinuity in the region where the more diffuse local maximum becomes dominant, illustrating a limitation of our focus on the global maximum.

Figure SI-12 compares the atom-averaged kinetic energy and delocalization length as functions of a. The kinetic energy initially decreases with a, but converges to an asymptotic value by $a \sim 10$ bohr. However, the atom-averaged delocalization length increases substantially up to $a \sim 20$ bohr, and decays rather slowly with further increases in a. This confirms that the atom-averaged delocalization length is relatively sensitive to small amounts of diffuse electron density.
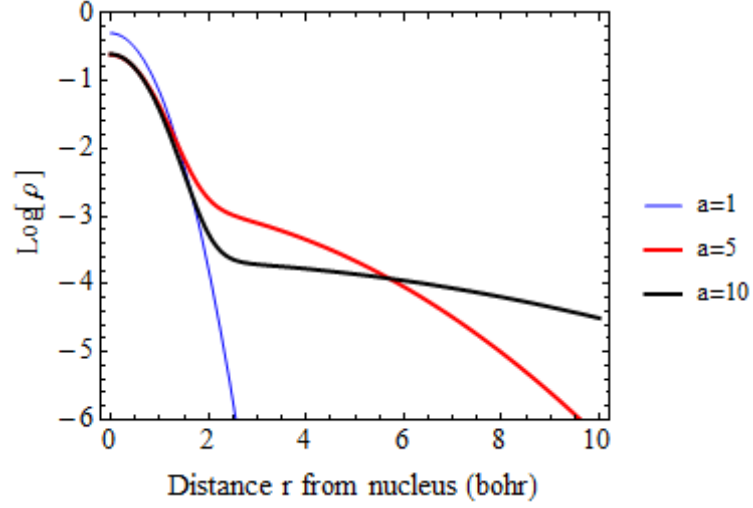
FIG. SI-10: Electron density $\rho(\vec{r})$ from Eq. SI-1, vs. distance r from nucleus, at several values of the diffuse basis function's radius a and $\lambda = 1$.
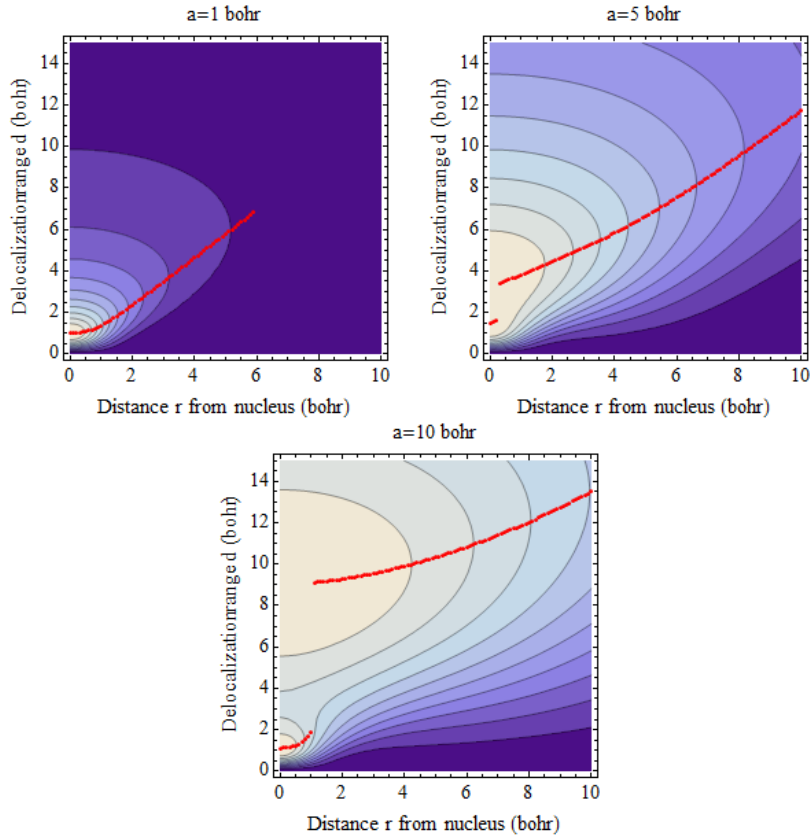

FIG. SI-11: Contour plots of $EDR(r; d)$ from Eq. SI-1, plotted vs. distance r from nucleus and delocalization length d, at several values of the diffuse basis function's radius a and $\lambda = 1$. Red lines denonte $D(r)$.
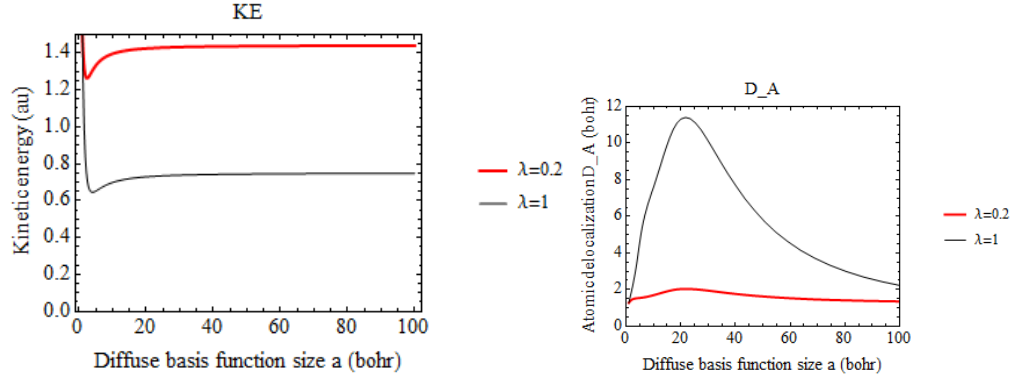
FIG. SI-12: Kinetic energy and atomic delocalization length D_A from Eq. SI-1, plotted vs. delocalized basis function size a. Results at two values of λ.