Nanoscale ultrasensing using a nonbonding plasmon resonance

Jer-Shing Huang,1,2,3* Gary Razinskas,4 Philipp Grimm,4 and Bert Hecht4,*

1 Leibniz Institute of Photonic Technology, Albert-Einstein-Str. 9, 07754 Jena, Germany
2 Research Center for Applied Sciences, Academia Sinica, 128 Sec. 2, Academia Road, Nankang District, Taipei 11529, Taiwan
3 Department of Electrophysics, National Chiao Tung University, Hsinchu 30010, Taiwan
4 Nano-Optics & Biophotonics Group, Department of Experimental Physics 5, & Röntgen Research Center for Complex Material Research (RCCM), Physics Institute, University of Würzburg, Am Hubland, 97074 Würzburg, Germany

Placing a plasmonic nanorod near the termination of a plasmonic nanowire dramatically changes the reflection of the wire’s guided mode. By carefully choosing the length of the nanorod, the reflectivity at the wire termination nearly vanishes due to destructive interference between the directly reflected wire mode and the infinite sum of the partial transmissions back into the wire of the reflected modes inside the nanorod. We show that this near-zero reflection condition corresponds to the so far overlooked nonbonding resonance which corresponds to a minimal coupling condition with extreme sensitivity to any changes in the nanorod’s local environment. We explicitly quantify the sensitivity of the nonbonding condition towards small local and global perturbations of the refractive index and outline a method to exploit the nonbonding condition for near-field ultrasensing.

Light can be guided by nanoscale metallic wires as surface plasmon polaritons.1-14 The complex propagation constant of the guided plasmon mode depends on the material and the geometry of the nanowire as well as the surrounding medium.2,4,6,11,12,15-17 At a wire termination, the guided mode is partially reflected and partially scattered into the far field. The reflection can be interpreted as being due to the impedance jump between the wire’s characteristic impedance $Z_0$ and a load impedance $Z_{load}$ embodied by the nanowire termination.12,18-21 The load impedance can be tailored by modifying the wire termination. Figure 1a depicts a simple modification, i.e. the addition of a short nanorod of the same cross section and variable length via a finite gap. By tuning the length of the nanorod, a condition of near-zero reflectivity can be obtained, at which the nanorod resonance seemingly absorbs all the power delivered via the nanowire mode but does hardly couple back to it. The corresponding length of the nanorod is very close to the resonance length of an isolated nanorod. The condition is therefore designated as “nonbonding” resonance condition. Around the nonbonding resonance, the phase change of the reflected wave is extremely steep and therefore sensitive to any small perturbations in the close vicinity of the nanorod. Typically, local sensing using single resonant plasmonic nanostructures is limited by the broad spectral linewidth and the correspondingly slow phase change. To circumvent this, extended arrays of plasmonic nanostructures have been employed to achieve narrow lattice resonances with steep phase responses.22-25 Yet the increased sensitivity comes at the cost of reduced spatial resolution. The nonbonding wire-rod system exhibits a sharp resonance and an extremely steep phase curve while maintaining a deep subwavelength footprint. These properties render the nonbonding wire-rod system highly advantageous for nanoscale integrated sensing purposes. Here, we study the origin of the nonbonding resonance condition and demonstrate its usability for ultrasensing applications. The novel sensing scheme may facilitate the detection of single molecular binding events.

The system under study consists of a gold nanowire with a circular cross section (diameter = 30 nm) in vacuum at 361.196 THz (wavelength = 830 nm). The wire is terminated by a hemispherical end cap. The propagation constant of the fundamental guided mode is solved using the finite-difference frequency-domain method (MODE Solutions, Lumerical Solutions Inc.).26 The dielectric function of gold is modeled using the data by Johnson and Christy.27 The obtained eigenmode is used as a source in three-dimensional finite-difference time-domain simulations (FDTD Solutions, Lumerical Solutions Inc.). The nanogap between the wire and the nanorod is fixed to 10 nm. Due to the relatively small wire diameter of 30 nm compared to the free-space wavelength (830 nm), the nanowire supports only the fundamental TM$_0$ eigenmode.9,17 The transverse mode profile is displayed in the inset of Fig. 1a. The complex propagation constant of the guided mode can be expressed as

$$k = \beta + ia$$

where $i$ is the imaginary unit, $\beta = 2\pi/\lambda_{eff}$ is the propagation constant with $\lambda_{eff}$ the effective wavelength, and $a$ is the field decay constant due to Ohmic losses. Taking plasmon reflection at the wire termination into account the electric near-field intensity distribution along the semi-infinite wire is20,21

$$|E(x)|^2 = |E_0[e^{i k x} + e^{ik(x-x_0)}e^{i k x_0}]|^2,$$

where $E_0$ is the initial amplitude of the mode, $x$ is the spatial coordinate in the propagation direction, $x_0$ is the distance be-
b) Standing wave patterns of electric field component normal to the wire surface are recorded for details. (c) Reflectivity amplitude (upper panel) and phase (bottom panel) as a function of the nanorod length. Vertical lines indicate arm lengths resulting in reflection minima. The red and dashed green horizontal lines mark the reflection amplitude and phase of a termination open to vacuum and a gap in an infinitely long wire.

The effect is most pronounced for a rod length of 153 nm for which only 5% of the incoming mode intensity is reflected. As the nanorod length increases, the second and third dips emerge at 350 nm and 548 nm. Those interference minima are significantly broader and less deep which is due to an increasing impact of propagation loss. A common feature of all reflection minima is that a portion of the power of the guided mode is effectively trapped on the nanorod, resulting in strongly enhanced local optical fields (see Fig. 1b).

Since we consider the nanorods as Fabry-Perot resonators for the guided TM\\textsubscript{0} wire plasmon modes it is instructive to compare the resonance of a nanorod attached to a nanowire (a wire-rod system) with that of a nanorod attached to an identical nanorod via a nanogap (a symmetric two-wire gap nanoantenna). The resonance condition of the nanorod can be characterized by the accumulated phase $F$ for one round trip in units of $2\pi$,

$$F = \frac{2L\beta + \theta_{r1} + \theta_{r2}}{2\pi} \quad (3)$$

where $L$ is the length of the cylindrical part of the nanorod, $\beta$ is the propagation constant of the TM\\textsubscript{0} wire plasmon mode and $\theta_{r1}$ and $\theta_{r2}$ are the reflection phases at the respective terminations including the hemispherical end caps. Resonances occur at integer $F$ values. Using $\beta$ and the reflection phases of Fig. 1c, $F$ can be calculated as a function of the rod length. The result is plotted in Fig. 2.

For the wire-rod system, the nanorod has one end open to vacuum and the other end facing the gap towards the nanowire. Increasing the rod length linearly increases $F$, resulting in one single resonance length at each integer $F$ (black trace in Fig. 2). For symmetric two-wire gap nanoantennas, the two identical nanorods have one end open to vacuum and the other facing an identical nanorod via a gap. The coupling of the two nanorods...
leads to a notable oscillation around each integer value of $F$. As a result, triples of resonant lengths are found for each integer $F$. Taking $F = 1$ as an example, only one resonance length is found at 153 nm for the wire-rod system but three resonant lengths are found at 136 nm, 153 nm and 173 nm for nanoantennas for the same resonance order. The shortest and longest rod lengths correspond to the arm lengths of the bonding and antibonding two-wire gap nanoantennas, respectively (supplemental material). The intermediate rod length (153 nm) coincides with the resonant length of a single nanorod in a vacuum (158 nm). In other words, in the wire-rod system, the resonance of the nanorod is not perturbed by the presence of the nanowire. This means that the nanorod is decoupled from the wire despite the very small size of the nanogap. We, therefore, call the nanorod at this length a “nonbonding” nanorod. Bonding and antibonding modes of two-wire gap nanoantennas have been extensively studied. However, the nonbonding condition corresponding to a condition of minimal coupling between the two identical nanorods has so far been overlooked. In the following, we discuss the significance of the nonbonding condition and theoretically demonstrate its application in ultrasensing.

![Graph showing F ratio as a function of length of a nanorod attached to a nanowire (black dots) and to an identical nanorod (grey squares) through a 10 nm gap. The latter finds three resonant lengths at each integer F, corresponding to the bonding, nonbonding and antibonding resonance.](image)

**FIG. 2 (color online).** $F$ ratio as a function of the length of a nanorod attached to a nanowire (black dots) and to an identical nanorod (grey squares) through a 10 nm gap. The latter finds three resonant lengths at each integer $F$, corresponding to the bonding, nonbonding and antibonding resonance.

In the nonbonding wire-rod system, the highly suppressed back coupling to the wire leads to effective trapping of the optical power on the nanorod and consequently to considerable field enhancement around the nanorod accompanied by an extremely steep phase change. To benchmark the sensitivity of the wire-rod system as a sensing element, in Fig. 3 we compare the reflection amplitude and phase of the TM$_0$ wire mode by a nonbonding termination (length = 153 nm) with the scattering of plane waves ($\lambda = 830$ nm) by a single nanorod in a vacuum (length = 158 nm). With the nonbonding nanorod, the reflection phase exhibits extremely steep variation around the minimum of the reflection amplitude (Fig. 3a). For the single nanorod in a vacuum, the scattering phase variation is rather moderate as expected from a harmonic resonator passing its resonance. Since the nonbonding resonance results in minimum reflection and dramatic changes of the phase, it is very sensitive to tiny changes in the local environment of the nanorod. We, therefore, propose using the combination of a nanowire with a nonbonding nanorod as an ultrasensitive local sensing device.

In a first demonstration, we show that a nonbonding wire-rod sensor is much more sensitive than a single isolated nanorod by placing a glass nanosphere (diameter = 20 nm) in its close vicinity. We scan the separation between nanosphere and nanorod (Fig. 4a) to obtain the reflection amplitude and phase at each separation. For a fair comparison of the sensitivity between the nonbonding wire-rod sensor and the single nanorod sensor, we evaluate the relative normalized change in the amplitude by $\Gamma_{\text{with sphere}}/\Gamma_{\text{without sphere}}$ and in the phase, we report the change in units of $2\pi$ by $\theta_{\text{with sphere}} - \theta_{\text{without sphere}}/\Gamma_{\text{without sphere}}$.

![Graph showing reflection amplitude and phase as a function of rod length.](image)

**FIG. 3 (color online).** (a) Reflection amplitude (blue) and phase (red) of the TM$_0$ wire plasmon mode as a function of the length of the nanorod attached to the wire termination via an air gap. The reflection phase exhibits an extremely steep slope at the reflection minimum at the rod length corresponding to the nonbonding resonance (153 nm). (b) Scattering cross section and phase of a single nanorod excited by a longitudinally polarized plane wave. The wavelength is 830 nm.

The relative normalized changes in reflection amplitude and phase are plotted in Figs. 4b and c, respectively. For a nonbonding nanorod-wire system, the relative changes in reflection amplitude and phase exhibit a pronounced increase for separations of less than 5 nm. This is in stark contrast to the scattering intensity and phase change of a resonant single nanorod, as
typically used in plasmonic sensing. Since the ultrahigh sensitivity is only found for separation below 5 nm, the ultrasensitive probe has a very small probe volume localized in the close vicinity of the nanorod, which makes the probe insensitive to matrix fluctuations outside the probe volume. Similarly, for surrounding index changes (Fig. 4d) the nonbonding wire-rod sensor again by far outperforms the single resonant nanorod. The relative reflection amplitude and phase in comparison with the scattering of a single nanorod are plotted in Figs. 4e and f. While the resonant single nanorod is rather insensitive to the surrounding index variation, the nonbonding wire-rod sensor shows extremely high sensitivity to the index change. We conceive that even attachment or detachment of single proteins should be detectable. \[32-34\]

Finally, we propose a method to experimentally observe the change of the reflection in the far field. As illustrated in Fig. 5, one may exploit the spin-orbit locking effect to launch the guided plasmonic mode in one direction and to detect the reflected mode. Two gold nanoparticles are placed close to the nanowire with a nonbonding termination. The distance between the two nanoparticles must be large enough to be resolved by an optical microscope. Right-handed circularly polarized light (CPL) at 830 nm will be focused onto the nanoparticle closer to the gap in order to launch the guided mode into one single propagation direction determined by the handedness of the CPL via spin-orbit locking. \[32-43\] The guided mode will propagate to the nanowire termination where it is fed into the nanorod with hardly any back reflection, as shown in Fig. 1b. Upon disturbance of the nonbonding condition, a backward propagating mode will be scattered first by the in-coupling nanoparticle and then the out-coupling nanoparticles. The scattered light is circularly polarized with opposite handedness because the propagation direction of the guided mode is reversed by the reflection. With this scheme, the detection will be nearly background free. To access the reflection phase, a reference beam must be introduced to interfere with the out-coupled left-handed CPL.

In conclusion, we present a new type of ultrasensitive near-field probe based on the so far overlooked nonbonding resonance. We present a semi-analytical Fabry-Pérot model to predict the arm length for bonding, nonbonding and antibonding modes of symmetric two-wire gap nanoantennas. The nonbonding resonance condition virtually decouples the nanorod from the feeding structure based on an extremely sensitive heterodyne destructive interference condition. The nonbonding resonance condition is therefore very sensitive to the local environment of the nanorod. Any tiny change of the local environment leads to very large variations in the reflection amplitude and even more so in the reflection phase. Therefore, a nanowire terminated by a nonbonding nanorod can serve as an ultrascope for near-field sensing. We also propose an experimentally realizable scheme to detect the reflection mode by exploiting the spin-orbit locking effect.

**ASSOCIATED CONTENT**

**Supporting Information.** Analytical model for the interference of the backward propagating modes. Simulated resonances of symmetric two-wire gap nanoantennas

**AUTHOR INFORMATION**

**Corresponding Author**

* E-mail: jer-shing.huang@leibniz-ipht.de
* E-mail: hecht@physik.uni-wuerzburg.de

**NOTES**

The authors declare no competing financial interest.
ACKNOWLEDGMENT

The authors acknowledge the financial support from the DFG via grants HU2626/3-1 and HE5618/6-1

REFERENCES

1.  L. Novotny and C. Hafner, Phys. Rev. E 50 (5), 4094-4106 (1994).
2.  J. Takahara, S. Yamagishi, H. Taki, A. Morimoto and T. Kobayashi, Opt. Lett. 22 (7), 475-477 (1997).
3.  R. M. Dickson and L. A. Lyon, J. Phys. Chem. B 104 (26), 6095-6098 (2000).
4.  H. Ditlacher, A. Hohenau, D. Wagner, U. Kreibig, M. Rogers, F. Hofer, F. R. Aussenegg and J. R. Krenn, Phys. Rev. Lett. 95 (25), 257402 (2005).
5.  A. V. Akimov, A. Mukherjee, C. L. Yu, D. E. Chang, A. S. Zibrov, P. R. Hemmer, H. Park and M. D. Lukin, Nature 450 (7168), 402-406 (2007).
6.  L. Novotny, Phys. Rev. Lett. 98 (26), 266802 (2007).
7.  G. W. Bryant, F. J. Garcia de Abajo and J. Aizpurua, Nano Lett. 8 (2), 631-636 (2008).
8.  J. Dorfmüller, R. Vogelgesang, R. T. Weitz, C. Rockstuhl, C. Etrich, T. Persch, F. Lederer and K. Kern, Nano Lett. 9 (6), 2372-2377 (2009).
9.  S. Zhang, H. Wei, K. Bao, U. Hakanson, N. J. Halas, P. Nordlander and H. Xu, Phys. Rev. Lett. 107 (9), 096801 (2011).
10. T. Shegai, V. D. Miljkovic, K. Bao, H. Xu, P. Nordlander, P. Johansson and M. Kall, Nano Lett. 11 (2), 706-711 (2011).
11. P. Biagioni, J.-S. Huang and B. Hecht, Rep. Prog. Phys. 75 (2), 024402 (2012).
12. Y.-T. Hung, C.-B. Huang and J.-S. Huang, Opt. Express 20 (18), 20342-20355 (2012).
13. P. Geisler, E. Krauss, G. Razinskas and B. Hecht, ACS Photon. 4 (4), 1615-1620 (2017).
14. H. Wei, D. Pan, S. Zhang, Z. Li, Q. Li, N. Liu, W. Wang and H. Xu, Chem. Rev. 118 (6), 2882-2926 (2018).
15. S. A. Maier, Springer Science & Business Media (2007).
16. E. Feigenbaum and M. Orenstein, Phys. Rev. Lett. 101 (16), 163902 (2008).
17. C. Rewitz, T. Keitzl, P. Tuchschner, J. S. Huang, P. Geisler, G. Razinskas, B. Hecht and T. Brixtner, Nano Lett. 12 (1), 45-49 (2012).
18. D. K. Cheng, Addison-Wesley Publishing Company (1989).
19. E. S. Barnard, J. S. White, A. Chandran and M. L. Brongersma, Opt. Express 16 (21), 16529-16537 (2008).
20. J.-S. Huang, T. Feichtner, P. Biagioni and B. Hecht, Nano Lett. 9 (5), 1897-1902 (2009).
21. G. Razinskas, P. Biagioni and B. Hecht, Sci. Rep. 8 (1), 1921 (2018).
22. P. Offermans, M. C. Schaafsma, S. R. Rodriguez, Y. Zhang, M. Crego-Calama, S. H. Brongersma and J. Gomez Rivas, ACS Nano 5 (6), 5151-5157 (2011).
23. R. R. Gutha, S. M. Sadeghi, C. Sharp and W. J. Wing, Nanotechnology 28 (35), 355504 (2017).
24. A. Danilov, G. Tselikov, F. Wu, V. G. Kravets, I. Ozerov, F. Bedu, A. N. Grigorenko and A. V. Kabashin, Biosens. Bioelectron. 104, 102-112 (2018).
25. V. G. Kravets, A. V. Kabashin, W. L. Barnes and A. N. Grigorenko, Chem. Rev. 118 (12), 5912-5951 (2018).
26. Z. Zhu and T. G. Brown, Opt. Express 10 (17), 853-864 (2002).
27. P. B. Johnson and R. W. Christy, Phys. Rev. B 6 (12), 4370-4379 (1972).
28. J.-S. Huang, J. Kern, P. Geisler, P. Weinmann, M. Kamp, A. Forchel, P. Biagioni and B. Hecht, Nano Lett. 10 (6), 2105-2110 (2010).
29. W.-L. Chen, F.-C. Lin, Y.-Y. Lee, F.-C. Li, Y.-M. Chang and J.-S. Huang, ACS Nano 8 (9), 9053-9062 (2014).
30. E. Prodan, C. Radloff, N. J. Halas and P. Nordlander, Science 302 (5644), 419-422 (2003).
31. A. M. Funston, C. Novo, T. J. Davis and P. Mulvaney, Nano Lett. 9 (4), 1651-1658 (2009).
32. I. Ament, J. Prasad, A. Henkel, S. Schmachtel and C. Sonnichen, Nano Lett. 12 (2), 1092-1095 (2012).
33. P. Zijlstra, P. M. Paulo and M. Orrit, Nat. Nanotech. 7 (6), 379-382 (2012).
34. V. R. Dantham, S. Holler, C. Barbret, D. Keng, V. Kolchenko and S. Arnold, Nano Lett. 13 (7), 3347-3351 (2013).
35. M. W. Knight, N. K. Grady, R. Bardhan, F. Hao, P. Nordlander and N. J. Halas, Nano Lett. 7 (8), 2346-2350 (2007).
36. X. Li, L. Huang, Q. Tan, B. Bai and G. Jin, Opt. Express 19 (7), 6541-6548 (2011).
37. F. J. Rodriguez-Fortuño, G. Marino, P. Ginzburg, D. O’Connor, A. Martinez, G. A. Wurtz and A. V. Zyazits, Science 340 (6130), 328 (2013).
38. J. Petersen, J. Volz and A. Rauschenbeutel, Science 346 (6205), 67 (2014).
39. D. O’Connor, P. Ginzburg, F. J. Rodriguez-Fortuño, G. A. Wurtz and A. V. Zyazits, Nat. Commun. 5, 5327 (2014).
40. S.-H. Gong, F. Alpeggiani, B. Sciaccia, E. C. Garnett and L. Kuipers, Science 359 (6374), 443 (2018).
41. T. Chervy, S. Azzini, E. Lorchat, S. Wang, Y. Gorodetski, J. A. Hutchison, S. Berciaud, T. W. Ebbesen and C. Genet, ACS Photon. 5 (4), 1281-1287 (2018).
42. M. Thomaschewski, Y. Yang, C. Wolff, A. S. Roberts and S. I. Bozhevolnyi, Nano Lett. 19 (2), 1166-1171 (2019).
43. E. Krauss, G. Razinskas, D. Köck, S. Grossmann and B. Hecht, Nano Lett. 19 (5), 3364-3369 (2019).
Nanoscale ultrasensing using a nonbonding plasmon resonance

Jer-Shing Huang,1,2,3* Gary Razinskas,4 Philipp Grimm,4 and Bert Hecht4,*

1 Leibniz Institute of Photonic Technology, Albert-Einstein-Str. 9, 07754 Jena, Germany
2 Research Center for Applied Sciences, Academia Sinica, 128 Sec. 2, Academia Road,
   Nankang District, Taipei 11529, Taiwan
3 Department of Electrophysics, National Chiao Tung University, Hsinchu 30010, Taiwan
4 Nano-Optics & Biophotonics Group, Department of Experimental Physics 5,
   & Röntgen Research Center for Complex Material Research (RCCM),
   Physics Institute, University of Würzburg, Am Hubland, 97074 Würzburg, Germany

I. Analytical model for the interference of the backward propagating modes

In this section, we model the reflection behavior of the wire-rod system. We consider interference effects of the direct reflection at the nanogap and the fields which are fed back to the wire across the gap after having undergone oscillations on the nanorod (Fig. S1(a)). The superposition of these contributions resulting in the total reflection \( R_{tot} \) reads

\[
R_{tot} = R_g + \frac{T_g}{R_g} \cdot \sum_{k=1}^{n} \left[ R_e R_g e^{2(-\alpha+i\beta)L_{net}} \right]^k.
\]  
(Eq. S1)

Here, \( R_g \) and \( T_g \) are coefficients for reflection and transmission across the gap in an infinitely long wire, respectively. \( R_e \) denotes the reflection at the end of the nanorod open to vacuum. The guided TM\(_0\) eigenmode is characterized by its propagation constant \( \beta \) and attenuation constant \( \alpha \). \( L_{net} \) is the net length of the nanorod, i.e. the length of its cylindrical part without the hemispherical endcaps and \( n \) represents the number of oscillation roundtrips on the nanorod. Since losses are already included in the attenuation constant, damping high-order oscillations accordingly, we consider \( n \to \infty \) and simplify the sum in (Eq. S1) using the limit of the geometric series:

\[
R_{tot} = R_g + \frac{T_g}{R_g} \cdot \left( \frac{1}{1-R_e R_g e^{2(-\alpha+i\beta)L_{net}}} - 1 \right)
\]  
(Eq. S2)

In Lumerical MODE solutions and FDTD solutions we determine the following parameter values (gap = 10 nm):

\[
R_g = 0.7998 \exp(i \ 1.1495 \ \text{rad})
\]
\[
R_e = 0.9492 \exp(i \ 1.0886 \ \text{rad})
\]
\[
\alpha = 3.90533 \cdot 10^{-4} \ \text{nm}^{-1}
\]
\[ \beta = 0.016078 \text{ nm}^{-1} \]

\[ |T_g| = 0.5579 \]

The \( \arg(T_g) \) is open for fitting the power series model (Eq. S2) to the reflection data obtained from FDTD simulations (Fig. 1c in the main text). The analytical result is shown in Figure S1. The power series model reproduces the pronounced minima in reflection amplitude and the steep jumps in reflection phase at the corresponding nonbonding rod lengths. From the fit we find \( \arg(T_g) = -0.3365 \text{ rad} \).

**Figure S1.** (a) Schematic illustration of the interference between the direct reflection and the power series of the fed back modes from the nanorod. (b) Reflection amplitude (upper panel) and phase (lower panel) of the wire-rod system. The total reflection is modeled by the interference of direct reflection at the gap and back-transmitted fields from the rod resonator. Black data points representing results from full FDTD simulations are taken from Figure 1c in the main text. The solid red line is the fit of the analytical power series model for infinite oscillation roundtrips (Eq. S2) to the numerical reflection coefficient. The pronounced features in total reflection are fully captured by the analytic approach.
II. Simulated resonances of symmetric two-wire gap nanoantennas

Figure S2. Simulated resonances of a series of single rods and gap nanoantennas as a function of the arm length. The bonding (black) and antibonding (red) resonances are obtained by exciting the antenna with a displaced dipole source and record the field at the end of the antenna, while the nonbonding resonance (blue) is obtained from a single rod. The simulated resonance wavelengths for the three lowest resonance orders are indicated by squares, circles, and triangles, respectively. Inset: Near-field intensity distribution in a cut mid-height through structures showing 1st order bonding (top), nonbonding (center), and antibonding (bottom) resonance, respectively.