Tuning Paramagnetic Spin Excitations of Single Adatoms

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We predict the existence of paramagnetic spin excitations (PSE) in nonmagnetic single adatoms. Our calculations demonstrate that PSE develop a well-defined structure in the meV region when the adatom’s Stoner criterion for magnetism is close to the critical point. We further reveal a subtle tunability and enhancement of PSE by external magnetic fields. Finally, we show how PSE can be detected as moving steps in the $dI/dV$ signal of inelastic scanning tunneling spectroscopy, opening a potential route for experimentally accessing electronic properties of nonmagnetic adatoms, such as the Stoner parameter.

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Single adatoms deposited on surfaces have become a prominent playground where theory and experiment can explore hand by hand a large variety of physical phenomena ranging from spin excitations [1–10] to magnetic exchange interactions [11–13], quantum spin decoherence [14–16], topological superconductivity [17–19], or the Kondo effect [20,21], among many others. Virtually all of these effects arise from the intricate interplay between the degrees of freedom of the adatom—charge, spin, or orbital momentum—and the electron and phonon bath of the substrate, a subject of heavy and ongoing investigation.

Noteworthily, magnetism plays a central role in fueling the interest for single adatoms, given that they represent the ultimate limit in the context of bit miniaturization in data storage devices. As a consequence, great efforts are being devoted to the search and characterization of elements that become magnetic when deposited on a substrate. Successful examples include, e.g., Fe and Co on Pt(111) [7,22], Fe on Cu(111) [6] as well as on Cu$_2$Ni/Cu(111) [23] and CuNi [1], Co on MgO(100) [24], and more recently Ho on MgO/Ag(100) [25], which all exhibit local magnetic moments greater than 2 $\mu_B$ and reveal clear signatures of magnetism that manifest either in a large magnetic anisotropy energy, steps in the $dI/dV$ signal related to spin excitations, or even remanence of the magnetic signal.

In this Letter, we propose and argue that even nominally nonmagnetic single adatoms can exhibit clear fingerprints of magnetism in the form of well-defined features in the spin-excitation spectrum, i.e., paramagnetic spin excitations (PSE). Interestingly, PSE are the analogs of so-called paramagnons first proposed by Doniach in 1967 [26] and first measured in bulk Pd nearly 50 years later by Doubble et al. [27] (see also Ref. [28] for recent calculations). In the context of Fermi liquid theory, these excitations can be viewed as persistent spin-fluctuation modes that can be activated by temperature and thus produce a measurable impact on properties such as specific heat or electron effective-mass enhancement [26,29]. Upon reducing the dimensionality of the system, here we show that PSE can be strongly enhanced due to the modified interplay between the two fundamental electronic properties involved, namely the Stoner exchange interaction and the adatom’s density of states (DOS) at the Fermi level. Importantly, this opens up unforeseen potential applications of nonmagnetic adatoms in nanotechnology, which encodes and manipulates information into excitation modes like PSE. In addition, our ab initio analysis based on time-dependent density functional theory (TDDFT) reveals that PSE are highly sensitive to externally applied magnetic fields and, furthermore, can exhibit a singular enhancement when the field approaches a critical regime. Motivated by these findings, we assess the impact of PSE on the $dI/dV$ signal as measured in inelastic scanning tunneling spectroscopy (ISTS) experiments, identifying clear signatures of magnetic response that allow us to distinguish these types of excitations from, e.g., phonons.

A central property for our discussion is the spin-excitation spectrum of nonmagnetic adatoms. Within the TDDFT formalism, this information is encoded into the longitudinal component of the enhanced spin susceptibility, $\chi(\omega)$, which is related to the response of the noninteracting Kohn-Sham (KS) system, $\chi_{KS}(\omega)$ [30]:

$$
\chi(\omega) = \frac{\chi_{KS}(\omega)}{1 - I_s \chi_{KS}(\omega)}.
$$

Above, $I_s$ denotes the so-called Stoner parameter, which plays the role of the exchange-correlation kernel in the adiabatic local spin-density approximation [31]. Noteworthily, the static limit of Eq. (1) recovers the standard Stoner theory that provides the well-known criterion for magnetism, i.e., $\chi(0) < 0 \Rightarrow I_s \rho_F > 1$, with $\rho_F$ the adatom’s DOS at the Fermi level and we used $\chi_{KS}(0) = \rho_F > 0$ [30]. In essence, the product $I_s \rho_F$ quantifies the competition between the exchange interaction, which enhances the tendency towards magnetism of electrons in localized orbitals, and substrate hybridization, which induces delocalization of the adatom’s electrons and therefore acts against magnetism, thus playing the role of the kinetic
energy in the standard Stoner theory. It is interesting to note that even if an adatom does not fulfill the Stoner criterion, it can still develop dynamical PSE provided the details of the electronic structure make the denominator of Eq. (1) vanishingly small at a finite frequency.

Let us begin our analysis by characterizing the set of 3$d$, 4$d$, and 5$d$ transition metal adatoms that could potentially exhibit PSE. For this purpose, in Fig. 1 we list several adatoms whose calculated Stoner products are below or slightly above 1; the calculations have been performed following the Korringa-Kohn-Rostoker Green function formalism [4,32,33] (see Supplemental Material [34] for technical details) and considering three different substrates, namely Ag(100), Cu(111), and MgO/Ag(100). As a general trend, our calculations show that the metallic substrates Ag(100) and Cu(111) host adatoms whose Stoner product is closer to the critical value 1 as compared to insulating MgO/Ag(100). This is mainly due to the small $\rho_F$ in the later, as tabulated in the Supplemental Material [34]. Among the two metallic substrates, Ag(100) hosts adatoms whose Stoner product are closest to 1, with $I_y \rho_F$ ranging between $\sim 1$ for Sc, Ir, Rh, and Ni adatoms. Therefore, throughout the work we will focus on discussing the Ag(100) substrate in detail, as it illustrates best our findings.

In Fig. 2 we illustrate the calculated spin-excitation spectra as given by $\text{Im}\chi(\omega)$ from Eq. (1), where all calculations were done considering the nonmagnetic ground state (see Supplemental Material [34] for technical details). Interestingly, Fig. 2 reveals peaklike structures resonating at frequencies below 100 meV for Rh, Ni, Ir, and Sc adatoms. This is exceptional, as most nonmagnetic elements exhibit a featureless spectrum owing to a complete overdamping of the excitations. Rh represents the most favorable case, displaying a well-defined peak at $\omega_{\text{res}} \sim 20$ meV and a width of $\Delta \sim 50$ meV, the associated lifetime being $\tau = \frac{\omega_{\text{res}}}{\Delta} \sim 30$ fs. It is noteworthy that both the lifetime and the height of the peak, the later being related to the intensity of the excitation, are only one order of magnitude smaller than those of usual transverse spin-excitations measured by ISTS in magnetic adatoms, such as Fe on Cu(111) [see, e.g., Refs. [6,40]]. On the other extreme, Pd in Fig. 2 shows a highly overdamped resonance at around 600 meV (see figure inset) whose intensity is an order of magnitude smaller than that of Rh. Therefore, our ab initio calculations reveal the existence of PSE whose resonance frequency and width vary strongly depending on the adatom.

Next, we focus on characterizing the physical mechanism behind PSE that allows an interpretation of the ab initio results displayed in Fig. 2. For this purpose, let us consider the frequency expansion of the paramagnetic KS spin response function up to linear order, i.e., $\chi^{KS}(\omega) = \rho_F + i \omega \alpha + O(\omega^2)$. One can show (see Supplemental Material [34]) that the linear expansion coefficient is well approximated by $\alpha \sim -\pi \rho_F^2 / 4$. Therefore, the spin-excitation spectrum within this approximation is given by a simple expression involving only the DOS at $E_F$ and the Stoner parameter:

$$\text{Im}\chi(\omega) = \frac{\pi}{4} \left( 1 - I_y \rho_F \right) \frac{\rho_F^2 \omega}{(\Delta_\omega \rho_F^2)^2 + (\frac{\pi}{4} I_y \rho_F^2 \omega)^2}. \quad (2)$$

By extracting $\rho_F$ and $I_y$ from our ab initio calculations, we have computed and displayed the expression predicted by Eq. (2) for each of the adatoms considered in Fig. 2 (see dashed lines). A comparison to the full ab initio calculations (solid lines) reveals a very good agreement for frequencies below 100 meV in the case of Rh, Ir, and Sc, where both the peak and width are properly described within $\lesssim 10\%$ relative error. This error is considerably larger in the case of Ni, indicating the importance of higher order expansion terms in $\omega$ for this case. Finally, the peak for Pd is far beyond the limit of small frequencies and therefore the approximation of Eq. (2) breaks down.

Proving Eq. (2) to be an accurate approximation of the full spin-excitation density given by Eq. (1) is extremely
convenient, as the former provides an analytical interpretation for the origin of PSE in terms of just $ρ_F$ and $I_s$, two basic electronic properties of adatoms. Indeed, the resonance frequency, linewidth, and amplitude of PSE predicted by Eq. (2) can be cast into simple expressions:

$$\omega_{\text{res}} = \frac{4}{\pi} \frac{|1 - I_sρ_F|}{I_sρ_F}, \quad Δ = 2\sqrt{3}ω_{\text{res}},$$

$$A = \text{Im} \chi(ω_{\text{res}}) = \frac{1}{2I_s|1 - I_sρ_F|}. \quad \quad (3)$$

Interestingly, a potential measurement of the above quantities would directly yield experimental estimates for $ρ_F$ and $I_s$. Upon closer inspection, one recognizes the Stoner product $I_sρ_F$ as the key quantity in Eq. (3); as $I_sρ_F → 1$ (i.e., ferromagnetic instability), the resonance frequency as well as the linewidth tend to zero while the intensity of PSE shows a singularity. This analysis offers therefore the interpretation we sought for, namely, that elements closer to the ferromagnetic instability show enhanced PSE, as it can be clearly checked from the comparison of Figs. 1 and 2.

We emphasize that the mechanism just described is fundamentally different from the one taking place in magnetic adatoms, where the resonance frequency of transverse spin excitations is settled by the spin-orbit interaction via the magnetic anisotropy energy [40].

Having exposed the origin of PSE in single adatoms, we focus next on assessing their potential impact on the $dI/dV$ signal as measured in ISTS experiments, the technique of choice for measuring magnetic excitations (see, e.g., Refs. [6,7,41]). The corresponding minimal setup is illustrated in Fig. 3(a), which displays a scanning tunneling microscope (STM) tip measuring the adatom’s excitations under an applied external magnetic field, denoted as $B$. We first notice that PSE respond to magnetic fields by shifting their resonance frequency. This is quantitatively demonstrated in Figs. 3(b) and 3(c), where the calculated spin-excitation spectra are shown for Rh and Ni adatoms,
respectively, under $B$ fields of $\sim 10$ T that are achievable in state-of-the-art laboratories (see, e.g., Refs. [7,24,25]). Noteworthily, while the PSE of Rh shifts towards larger frequencies as $B$ is increased [see Fig. 3(b)], the PSE of Ni exhibits the opposite behavior [see Fig. 3(c)]. This difference arises from the fact that magnetic fields induce an effective modification of Stoner product, i.e., $I_s \rho_F \to \xi(B)I_s \rho_F$, where $\xi(B)$ is a term that depends both on the magnetic field as well as on the adatom’s electronic structure (see Supplemental Material [34]). In particular, the details of the later make $\xi(B) > 1$ for Ni while $\xi(B) < 1$ for Rh, leading to the aforementioned divergent responses in accordance with Eq. (3).

Remarkably, when strong enough magnetic fields are applied to Ni, the modified Stoner criterion can be tuned towards the critical point, as shown in Fig. 3(d). A consequence, the PSE of Ni exhibits the opposite behavior [see Fig. 3(c)]. When larger magnetic fields are applied, as illustrated in Fig. 3(f) for the case of Ni, the critical behavior of the PSE [see Fig. 3(d)] translates into a clear maximum at the value of the critical field, where $\text{Im}\Sigma(V_F)$ increases by an order of magnitude.

The presence of PSE has a broad effect on the renormalization of the DOS at the vacuum, where ISTS tips measure the signal. In particular, the energy derivative of the renormalized DOS (dDOS) is a quantity that is linked to the $d^2I/dV^2$ curve measured by ISTS [45]. The former quantity is displayed in Fig. 3(g) for Rh, where the magnetic field dependence is clearly visible. Noteworthily, our calculations demonstrate that the tunneling electrons from the tip are able to trigger the PSE, leading to a peak in the meV region that, furthermore, reacts to external magnetic fields by shifting its resonance frequency as well as substantially modifying its intensity. We also note the strong asymmetric distribution between positive and negative frequencies, a feature that emerges from the background electronic structure [45] and is commonly present in $d^2I/dV^2$ curves measured on magnetic adatoms (see, e.g., Refs. [6,7,46–48]). On the other hand, when Ni is driven into the critical regime as in Fig. 3(h), our calculations reveal a huge change of the signal’s intensity as the PSE approaches the critical point. Our analysis therefore shows that magnetism offers a prime way of manipulating PSE, enabling us to discern them from other excitations of similar energy but nonmagnetic origin, such as phonons.

In conclusion, we have proposed and argued a means of detecting spin excitations in nonmagnetic single adatoms. We have shown that such excitations can develop well-defined peaks in the meV region, their main characteristics being determined by two fundamental electronic properties, namely, the Stoner parameter and the DOS at the Fermi level. Our analysis based on TDDFT has further revealed a pronounced dependence of PSE on externally applied magnetic fields, exhibiting the atomic analog of a quantum phase transition as the field approaches the critical value. This remarkable feature is likely to have strong effects in processes where a substantial magnetic moment is induced in nonmagnetic adatoms, e.g., when magnetic atoms are coupled to them via the proximity effect. Finally, we have simulated ab initio the impact of PSE on the $d^2I/dV^2$ curve measured in state-of-the-art ISTS experiments, revealing that PSE can be triggered by tunneling electrons and, furthermore, exhibit a clear response to magnetic fields. Thus, besides opening up potential applications for nonmagnetic adatoms, our analysis offers a route for experimentally accessing their fundamental electronic properties, such as the Stoner parameter.
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Note added in the proof.—In the recent work of Ref. [49], the conductance associated to a single Pd adatom deposited on Pd(111) has been experimentally measured and interpreted as being strongly affected by paramagnon scattering.

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[1] C. F. Hirjibehedin, C.-Y. Lin, A. F. Otte, M. Ternes, C. P. Lutz, B. A. Jones, and A. J. Heinrich, Science 317, 1199 (2007).
[2] J. Fernández-Rossier, Phys. Rev. Lett. 102, 256802 (2009).
[3] N. Lorente and J.-P. Gauyacq, Phys. Rev. Lett. 103, 176601 (2009).
[4] S. Lounis, A. T. Costa, R. B. Muniz, and D. L. Mills, Phys. Rev. Lett. 105, 187205 (2010).
[5] L. Zhou, J. Wiebe, S. Lounis, E. Vedmedenko, F. Meier, S. Blügel, P. H. Dederichs, and R. Wiesendanger, Nat. Phys. 6, 187 (2010).
[6] A. A. Khajetoorians, S. Lounis, B. Chilian, A. T. Costa, L. Zhou, D. L. Mills, J. Wiebe, and R. Wiesendanger, Phys. Rev. Lett. 106, 037205 (2011).
[7] A. A. Khajetoorians, T. Schlenk, B. Schweflinghaus, M. dos Santos Dias, M. Steinbrecher, M. Bouhassoune, S. Lounis, J. Wiebe, and R. Wiesendanger, Phys. Rev. Lett. 111, 157204 (2013).
[8] M. Ternes, New J. Phys. 17, 063016 (2015).
[9] A. A. Khajetoorians, M. Steinbrecher, M. Ternes, M. Bouhassoune, M. d. S. Dias, S. Lounis, J. Wiebe, and R. Wiesendanger, Nat. Commun. 7, 10620 (2016).
[10] J. Ibáñez-Azpiroz, M. dos Santos Dias, S. Blügel, and S. Lounis, Nano Lett. 16, 4305 (2016).
[11] J. C. Oberg, M. R. Calvo, F. Delgado, M. Moro-Lagares, D. Serrate, D. Jacob, J. Fernández-Rossier, and C. F. Hirjibehedin, Nat. Nanotechnol. 9, 64 (2014).
[12] S. Yan, D.-J. Choi, B. Jacob A. J., S. Rolf-Pissarczyk, and S. Loth, Nat. Nanotechnol. 10, 40 (2015).
[13] A. Stróżeczka, A. Eiguren, and J. I. Pascual, Phys. Rev. Lett. 107, 186805 (2011).
[14] B. Bryant, R. Toskovic, A. Ferrn, J. L. Lado, A. Spinelli, J. Fernández-Rossier, and A. F. Otte, Nano Lett. 15, 6542 (2015).
[15] S. Baumann, W. Paul, T. Choi, C. P. Lutz, A. Ardavan, and A. J. Heinrich, Science 350, 417 (2015).
[16] F. Delgado and J. Fernández-Rossier, Prog. Surf. Sci. 92, 40 (2017).
[17] S. Nadj-Perge, I. K. Drozdov, J. Li, H. Chen, S. Jeon, J. Seo, A. H. MacDonald, B. A. Bernevig, and A. Yazdani, Science 346, 602 (2014).
[18] B. Braunecker and P. Simon, Phys. Rev. Lett. 111, 147202 (2013).
[19] M. M. Vazifeh and M. Franz, Phys. Rev. Lett. 111, 206802 (2013).
[20] M. Ternes, A. J. Heinrich, and W.-D. Schneider, J. Phys. Condens. Matter 21, 053001 (2009).
[21] K. von Bergmann, M. Ternes, S. Loth, C. P. Lutz, and A. J. Heinrich, Phys. Rev. Lett. 114, 076601 (2015).
[22] P. Gambardella, S. Rusponi, M. Veronesi, S. D. H. Cesi, C. Grazioli, A. Dallmeyer, I. Cabria, R. Zeller, P. H. Dederichs, K. Kern et al., Science 300, 1130 (2003).
[23] B. Bryant, A. Spinelli, J. J. T. Wagenaar, M. Gerrits, and A. F. Otte, Phys. Rev. Lett. 111, 127203 (2013).
[24] I. G. Rau, S. Baumann, S. Rusponi, F. Donati, S. Steapanow, L. Gragnaniello, J. Dreiser, C. Piamonteze, F. Nolting, S. Gangopadhyay et al., Science 344, 988 (2014).
[25] F. Donati, S. Rusponi, S. Steapanow, C. Wckerlin, A. Singha, L. Persichetti, R. Baltic, K. Diller, F. Patthey, E. Fernandes et al., Science 352, 318 (2016).
[26] S. Doniach, Proc. Phys. Soc. London 91, 86 (1967).
[27] R. Doubble, S. M. Hayden, P. Dai, H. A. Mook, J. R. Thompson, and C. D. Frost, Phys. Rev. Lett. 105, 027207 (2010).
[28] J. B. Staunton, J. Poulter, B. Ginatempo, E. Bruno, and D. D. Johnson, Phys. Rev. B 62, 1075 (2000).
[29] G. G. Lonzarich and L. Taillefer, J. Phys. C 18, 4339 (1985).
[30] A. Aguayo, I. I. Mazin, and D. J. Singh, Phys. Rev. Lett. 92, 147201 (2004).
[31] S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. 58, 1200 (1980).
[32] N. Papanikolaou, R. Zeller, and P. H. Dederichs, J. Physics Cond. Matter 14, 2799 (2002).
[33] S. Lounis, A. T. Costa, R. B. Muniz, and D. L. Mills, Phys. Rev. B 83, 035109 (2011).
[34] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.119.017203, which includes Refs. [35–39], for computational details regarding DFT and TDDFT calculations, additional electronic properties of adatoms on Ag(100) and MgO/Ag(100), technical details on the calculation of the longitudinal KS spin-susceptibility and its frequency expansion.
[35] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, Davide Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo et al., J. Phys. Cond. Matter 21, 395502 (2009).
[36] J. F. Janak, Phys. Rev. B 16, 255 (1977).
[37] B. Lazarovits, L. Szunyogh, and P. Weinberger, Phys. Rev. B 65, 104441 (2002).
[38] H. Beckmann and G. Bergmann, Phys. Rev. B 55, 14350 (1997).
[39] K. Wildberger, P. Lang, R. Zeller, and P. H. Dederichs, Phys. Rev. B 52, 11502 (1995).
[40] M. dos Santos Dias, B. Schweflinghaus, S. Blügel, and S. Lounis, Phys. Rev. B 91, 075405 (2015).
[41] M. Steinbrecher, A. Sonntag, M. d. S. Dias, M. Bouhassoune, S. Lounis, J. Wiebe, R. Wiesendanger, and A. A. Khajetoorians, Nat. Commun. 7, 10454 (2016).
[42] For externally applied \( B = 517 \) T the magnetic moment of Ni is \( m = 0.29 \mu_B \), while a Fe adatom placed as a second...
nearest neighbor induces a magnetic moment on Ni of $m = 0.51 \mu_B$.

[43] J. Tersoff and D. R. Hamann, Phys. Rev. Lett. 50, 1998 (1983).

[44] D. Wortmann, S. Heinze, P. Kurz, G. Bihlmayer, and S. Blügel, Phys. Rev. Lett. 86, 4132 (2001).

[45] B. Schweflinghaus, M. dos Santos Dias, A. T. Costa, and S. Lounis, Phys. Rev. B 89, 235439 (2014).

[46] A. J. Heinrich, J. A. Gupta, C. P. Lutz, and D. M. Eigler, Science 306, 466 (2004).

[47] S. Holzberger, T. Schuh, S. Blügel, S. Lounis, and W. Wulfhekel, Phys. Rev. Lett. 110, 157206 (2013).

[48] S. Baumann, F. Donati, S. Stepanow, S. Rusponi, W. Paul, S. Gangopadhyay, I.G. Rau, G.E. Pacchioni, L. Gragnaniello, M. Pivotta et al., Phys. Rev. Lett. 115, 237202 (2015).

[49] V. Schendel, C. Barreteau, M. Brandbyge, B. Borca, I. Pentegov, U. Schlickum, M. Ternes, P. Wahl, and K. Kern, arXiv:1702.02407.