Numerical renormalization group calculations of ground-state energy: Application to correlation effects in the adsorption of magnetic impurities on metal surfaces

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The ground-state energy of a quantum impurity model can be calculated using the numerical renormalization group with a modified discretization scheme, with sufficient accuracy to reliably extract physical information about the system. The approach is applied to study binding of magnetic adsorbates modeled by the Anderson-Newns model for chemisorption on metal surfaces. The correlation energy is largest in the valence-fluctuation regime; in the strong-coupling (Kondo) regime the Kondo-singlet formation energy is found to be only a minor contribution. As an application of the method to more difficult surface-science problems, we study the binding energy of a magnetic atom adsorbed near a step edge on a surface with a strongly modulated surface-state electron density. The zero-temperature magnetic susceptibility is determined from the field dependence of the binding energy, thereby providing an independent result for the Kondo temperature T_K, which agrees very well with the T_K extracted from a thermodynamic calculation.

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The magnetism of nanoscopic objects supported on surfaces is of great current interest due to possible applications in the ultradense data storage. The magnetic properties of adsorbates can now be studied on the single-atom level using scanning tunneling microscopes (STM) (Ref. 1). Adsorbed atoms attach to metal surfaces by forming strong (covalent) bonds in a process named chemisorption.[2,3] The chemisorption controls the valence (and thus the magnetic moment) of magnetic adsorbates, it can lead to adsorbate-induced restructuring of surfaces, it affects superlattice growth, chemical reactions (catalysis), and other surface phenomena.[3] Using an STM, adsorbed atoms may be manipulated to form artificial nanostructures.[4] For successful manipulation of atomic-scale objects, it is crucial to understand the binding properties of adsorbates, i.e., to know the potential-energy surface as a function of the position of the adsorbate.[2]

A highly simplified model for studying the chemisorption is the Anderson-Newns model:[5,6] $H=H_{\text{band}}+H_{\text{imp}}+H_c$ with

$$H_{\text{band}}=\sum_{k,\sigma\in\{\uparrow,\downarrow\}}\epsilon_k c^\dagger_{k\sigma}c_{k\sigma},$$

$$H_{\text{imp}}=\sum_{\sigma\in\{\uparrow,\downarrow\}}\epsilon n_\sigma+Un_\uparrow n_\downarrow,$$

$$H_{\text{hyb}}=\sum_{k,\sigma\in\{\uparrow,\downarrow\}}V_k(c^\dagger_{k\sigma}d_\sigma+d^\dagger_\sigma c_{k\sigma}). \tag{1}$$

H_{band} describes the continuum of conduction-band electrons with dispersion ϵ_k, H_{imp} corresponds to an adsorbate level with energy ϵ, and electron-electron repulsion U ($n_\sigma=d^\dagger_\sigma d_\sigma$ is the level occupancy operator), while H_{hyb} defines the hybridization which can be fully characterized by the function $\Gamma(\omega)=\Sigma_k|V_k|^2\delta(\omega-\epsilon_k)$. The adsorbate binding energy ΔE is defined as the difference between the ground-state energy of the system described by the full Hamiltonian H and the ground-state energy of the decoupled system with $H_{\text{hyb}}\equiv 0$ (i.e., the limit where the atom is far away from the surface). While the Anderson-Newns model was originally intended to describe binding of hydrogen and alkali atoms, some properties of magnetic adsorbates can also be studied within a single-orbital approximation.[7] General binding properties can be determined qualitatively correctly using the unrestricted Hartree-Fock (HF) method,[6] while the contributions due to correlations can be calculated variationally.[8] A method which could very accurately solve the problem in full generality for arbitrary energy-dependent $\Gamma(\omega)$ and for arbitrarily large interaction strength U has been, however, lacking. In this work, it is shown that the binding energy can be calculated with an excellent accuracy using the numerical renormalization group (NRG) (Refs. 9–11).

The NRG consists of a logarithmic discretization of H_{band} into intervals $[\Lambda^{-(j+1)}:\Lambda^{-j}]$ with $\Lambda>1$ followed by a mapping to an effective one-dimensional tight-binding Hamiltonian with exponentially decreasing hopping constants $\propto\Lambda^{-i/2}$ and an iterative diagonalization, where one further site is taken into account at each step. At each iteration i, the calculated excitation spectrum is shifted by subtracting the lowest eigenvalue E_i from all others. The series

$$E_{\text{NRG}}=\sum_{i=0}^{\infty}E_i \tag{2}$$

is the ground-state energy of the effective Hamiltonian. To improve the results, several independent NRG calculations are performed for interleaved discretization meshes shifted by Λ^{1-z} with $z\in(0:1]$ and the final result is obtained as an average over all z (Refs. 12 and 13). To the best knowledge of the author, the quantity E_{NRG} has never been used to extract physical information about the system, presumably, due to poor convergence properties and systematic errors of the conventional discretization scheme. These deficiencies of NRG were recently surmounted by a different discretization approach[14,15] which consists of solving the differential equation

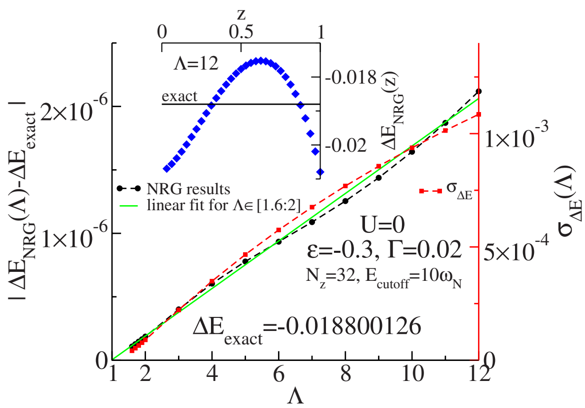

FIG. 1. (Color online) Λ dependence of the calculated binding energy of a noninteracting adsorbate. Exact binding energy ΔE_{exact} is subtracted from the numerical results $\Delta E_{\text{NRG}}(\Lambda)$ (circles). Full line is a linear fit to results in the interval $\Lambda \in [1.6:2]$. The error of the extrapolated $\Lambda \to 1$ value is 3.3×10^{-9}. The standard deviation $\sigma_{\Delta E}$ characterizes the spread of the results for different parameters z. An example of $\Delta E_{\text{NRG}}(z)$ for $\Lambda=12$ is shown in the inset. $N_z=32$ different values of z were used, while the parameter $E_{\text{cutoff}}=10\omega_N$ defines the truncation cutoff in the NRG iteration (Ref. 14).

$$\frac{d\mathcal{E}(x)}{dx} = \frac{\int_{\epsilon(x)}^{\epsilon(x+1)} \Gamma(\omega) d\omega}{\Gamma[\mathcal{E}(x)]}, \tag{3}$$

where the function $\mathcal{E}(x)$ with $x=j+z$ yields the discretization coefficients for each interval j and each parameter z; the function $\epsilon(x)$ defines the discretization grid.[15]

We first consider the binding of a noninteracting adsorbate with $U=0$. In this case, the binding energy can be calculated numerically to arbitrary precision by a simple quadrature [Eq. (39) in Ref. 6]. For simplicity, we first consider a constant hybridization function $\Gamma(\omega) \equiv \Gamma$ for $\omega \in [-1:1]$ and zero otherwise. By comparing the NRG results with the exact value for a range of discretization parameters Λ (Fig. 1), we find that the binding energies are calculated with high accuracy even at $\Lambda=12$; for $\Lambda=2$ the error is 2×10^{-7}. If bare model parameters (bandwidth, ϵ, and U) are on the order of the eV, this magnitude of the error implies that it is possible to determine the binding energy with μeV accuracy. The spread of the results $\Delta E_{\text{NRG}}(z)$ for different values of z, as measured by the standard deviation $\sigma_{\Delta E}$ in Fig. 1, is not an indication of the error committed but rather contains physically relevant information about the effects of the hybridization. The z averaging is thus an essential element of the binding-energy calculation and not merely an *ad hoc* procedure to accelerate the convergence.

At large Λ, the error can be decreased somewhat by increasing N_z, but the improvement is minor. A systematic improvement by 1 order of the magnitude can, however, be obtained by the interpolation between the data points followed by an integration over z on the interval [0:1]. The error is thereby reduced to 3×10^{-7} even at $\Lambda=12$ with no additional calculations. (There is actually no need to use a uniform mesh of parameters z; it is more economical to choose the z values as the quadrature nodes.) Using conventional discretization schemes, the errors are larger by orders of magnitude and even the extrapolated $\Lambda \to 1$ value disagrees with the exact result by 3×10^{-4}; this corresponds to an error on the order of meV, which is barely acceptable especially when small effects are considered, for example, in possible applications to long-range adsorbate-adsorbate interactions.[16] The use of the improved discretization scheme from Ref. 14 is thus crucial and, furthermore, the possibility of obtaining reasonably accurate results even at large Λ implies that calculations can be performed very efficiently.

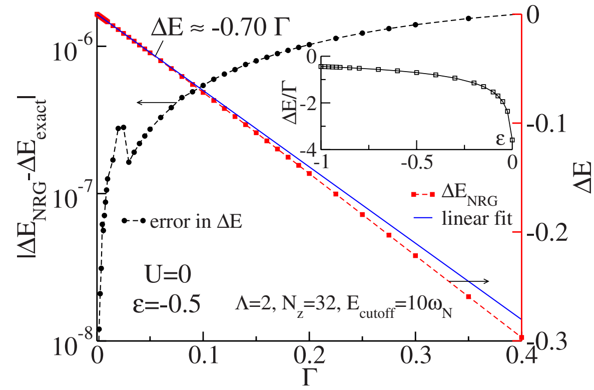

FIG. 2. (Color online) Binding energy ΔE (right vertical axis) and numerical error $\Delta E_{\text{NRG}} - \Delta E_{\text{exact}}$ (left vertical axis) of a noninteracting adsorbate as a function of the hybridization Γ. The proportionality coefficient $\Delta E / \Gamma = -0.70$ is extracted in the interval $\Gamma \in [0:0.01]$. For reference, the inset shows $\Delta E / \Gamma$ as a function of ϵ.

For large hybridization Γ, the adsorbate perturbs the conductance band more strongly. In NRG calculations, this is of particular concern since a finite representation of the band is used; thus finite-size effects are expected to become sizable. We find, however, that at $\Lambda=2$ the error is bounded by 1.7×10^{-6} for all Γ in the interval [0:0.4] (Fig. 2). The binding energy ΔE is linear in Γ to a good approximation and the coefficient of proportionality increases in absolute value as ϵ approaches the Fermi level (see the inset in Fig. 2), where the hybridization is more effective in binding the adsorbate. The adsorbate tends to form a bond with the substrate by sharing an electron with the conductance-band states. This process is more efficient when states in the vicinity of the Fermi level are involved since their occupancy can be inexpensively changed by the hybridization. This is similar to bond formation in two-atom molecules, where the binding energy is largest when the atomic levels are aligned.

We now study the full Anderson-Newns model with finite interaction U and make comparison with the mean-field results obtained using the unrestricted HF method [which neglects correlation effects (see also Ref. 8)]. The binding energy reaches its highest absolute value for $\epsilon+U=0$ when the single-particle level for an additional electron crosses the Fermi level [Fig. 3(a)]. This behavior is similar to that of the noninteracting model. The binding energy is large when the charge fluctuates strongly. Both NRG and Hartree-Fock give the same qualitative features, but it is found that HF underestimates binding. The additional binding energy can be de-

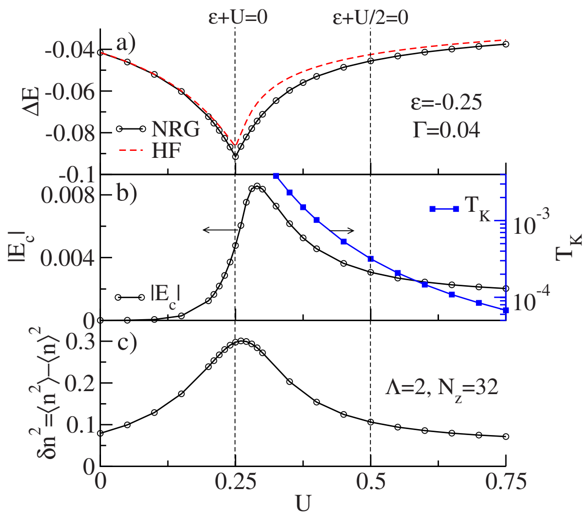

FIG. 3. (Color online) (a) Binding energy, (b) correlation energy $E_c = \Delta E - \Delta E_{\mathrm{HF}}$, Kondo temperature T_K (right vertical axis), and (c) charge fluctuations of the single-impurity Anderson model as a function of the electron-electron interaction U. The Kondo temperature is extracted from the thermodynamic properties of the model according to Wilson's prescription $k_B T_K \chi_{\mathrm{imp}}(k_B T_K)/(g\mu_B)^2 = 0.07$, where χ_{imp} is the impurity magnetic susceptibility (Ref. 9).

fined as the "correlation energy:" $E_c = \Delta E - \Delta E_{\mathrm{HF}}$. The correlation energy is largest in the valence-fluctuation regime for $\epsilon + U \approx \Gamma$ [see Fig. 3(b)]. At this point, the local moment begins to form [see the decreasing charge fluctuations δn^2 in Fig. 3(c) for increasing U] and the energy scale of magnetic correlations (the nascent Kondo regime) is the highest [see the Kondo temperature T_K in Fig. 3(b)]. The "Kondo-singlet formation energy" on the order of T_K does not account for the totality of the correlation energy. It is only a small fraction, in particular, in the large-U limit where the Kondo temperature is strongly suppressed. The most important contribution to the correlation energy thus stems from local charge correlations rather than from extended Kondo correlations.

The energy gain due to Kondo correlations is lost in a strong magnetic field (see Fig. 4). The quadratic reduction for low fields ($g\mu_B B \ll k_B T_K$) is expected due to finite spin

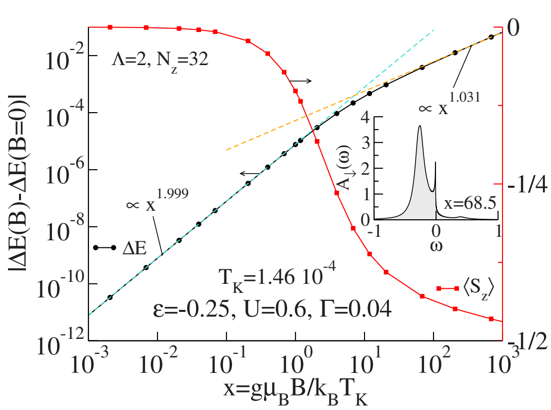

FIG. 4. (Color online) Binding energy and spin polarization of a magnetic adsorbate in an external magnetic field (expressed in reduced units of $x = g\mu_B B/k_B T_K$). The inset shows the spin-resolved impurity-spectral function in a strong field.

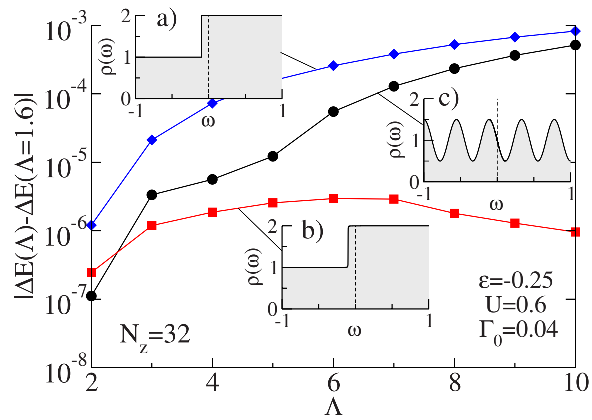

FIG. 5. (Color online) Λ dependence of the binding energy of a magnetic adsorbate hybridized to a band with energy-dependent density of states $\rho(\omega)$. The hybridization function is $\Gamma(\omega) = \Gamma_0 \rho(\omega)$ with (a) sharp-step function $\rho(\omega) = 1 + \theta(\omega - \omega_0)$ with $\omega_0 = -0.1$, (b) rounded-step function $\rho(\omega) = 1 + \{1/2 + (1/\pi)\tan^{-1}[\pi(\omega - \omega_0)/\Delta]\}$, where $\Delta = 0.001$, and (c) oscillatory $\rho(\omega) = 1 + (1/2)\cos[(9/2)\pi(1+\omega)]$. The $\Lambda = 1.6$ results are used as reference values and subtracted from $\Delta E(\Lambda)$.

susceptibility at zero temperature in the strong-coupling regime.[9] From the prefactor, we can extract the zero-temperature magnetic susceptibility

$$\chi(T=0) = \frac{W(g\mu_B)^2}{4\pi k_B T_K}, \tag{4}$$

where $W \approx 1.290\,26$ is the Wilson number.[9,17] From $\chi(T=0)$, we then obtain a value $T_K' = 1.43 \times 10^{-4}$ for the Kondo temperature, which differs from the value of $T_K = 1.46 \times 10^{-4}$ determined in a thermodynamic calculation of magnetic susceptibility by $<3\%$. Considering that the values are obtained using entirely independent procedures, their close agreement is an exceptional confirmation of the method. The remaining small discrepancy stems mostly from the error associated with obtaining the coefficient of the B^2 contribution to the total energy in the limit of very small magnetic fields. For large fields ($g\mu_B B \gg k_B T_K$), the Zeeman effect takes over and the variation in ΔE is approximately linear.

Albeit constant hybridization is a convenient simplification, in realistic problems $\Gamma(\omega)$ is strongly energy dependent. Three forms are considered here: sharp- and rounded-step functions and an oscillatory function. The convergence with Λ depends significantly on the form (see Fig. 5); while the error remains approximately constant at $\approx 10^{-6}$ for the rounded-step function, it increases significantly for the sharp-step and oscillatory function. As expected, sharp discontinuities and variations that occur over extended energy intervals lead to larger errors than smooth localized changes.

The capabilities of the method for problems with strongly energy-dependent hybridization are demonstrated with the example of a magnetic adsorbate in the vicinity of a step edge on a surface supporting a surface-state band. The adsorbate hybridizes both with the bulk states via Γ_b (which will be assumed not to vary with energy) and with surface states via Γ_s. On a clean flat surface, $\Gamma(\omega)=\Gamma_b+\Gamma_s\theta(\omega-\omega_0)$, where ω_0 is the onset of the surface-state band. More interesting situation occurs when the adsorbate is adsorbed near a step edge, where the local density of states of surface-state electrons is modulated by standing waves. Modeling the step edge as a hard-wall potential, the energy-resolved charge density is $\delta n(x,\omega)\propto 1-J_0[2k(\omega)x]$, where J_0 is the Bessel function, $k(\omega)$ is the wave number at energy ω, and x is the distance from the step edge. Modeling the surface-state electrons as free electrons with effective mass m^*, we have $k(\omega)=[(2m^*/\hbar)(\omega-\omega_0)]^{1/2}$. The hybridization function is thus

$$\Gamma(\omega)=\Gamma_b+\Gamma_s\theta(\omega-\omega_0)\{1-J_0[2k(\omega)x]\}. \tag{5}$$

While it is by now established that for magnetic impurities on noble-metal surfaces $\Gamma_s \ll \Gamma_b$ (Refs. 18 and 19), we will nevertheless take a greatly exaggerated ratio $\Gamma_s/\Gamma_b=1$ to accentuate the effect of the energy dependence of $\Gamma(\omega)$. In fact, on surfaces with giant Friedel oscillations,[20] such ratio might be realistic.

The adsorbate properties reflect the oscillatory features in $\Gamma(\omega)$ (see Fig. 6). The Kondo temperature is strongly correlated with the variation in Γ at the Fermi level and it can be well described by a cosine function with constant phase shift δ_{T_K} multiplied by some envelope function which is—to a good approximation—a power-law decay $1/x^{1.16}$. The binding energy, however, exhibits some additional structure, in particular, for low values of x. (This is not a numerical artifact: the same result is obtained for other choices of NRG parameters.) Qualitatively, similar features are visible in the adsorbate level occupancy $\langle n\rangle$ but at shifted positions x. The origin of these effects is thus in the details of the energy dependence of $\Gamma(\omega)$ over a wide energy interval (i.e., on the atomic scale of ϵ and U). This is unlike the Kondo temperature, which depends mostly on the values of $\Gamma(\omega)$ in the narrow interval on the scale of T_K itself and therefore simply follows the variation in $\Gamma(\omega=0)$. It may be noted that strong binding corresponds to high Kondo temperature and that variations in ΔE and T_K are on the same order of magnitude,

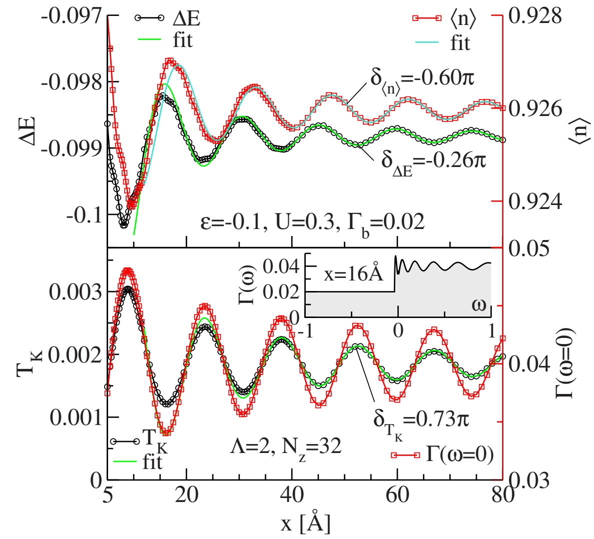

FIG. 6. (Color online) Properties of a magnetic adsorbate on a surface at a distance of x from a step edge modeled as a hard-wall potential scatterer. Fitting by oscillatory power-law functions $A+B\cos(2k_Fx+\delta)/x^\alpha$ provides the phase shifts δ (shown in the figure) and decay constants α: the binding energy ΔE decays as $1/x^{3/2}$, the occupancy as $1/x^{1.19}$, and the Kondo temperature as $1/x^{1.16}$. The fitting procedure was performed with the data in the asymptotic region $x\in[40:80]$ Å. The inset shows the hybridization function at $x=16$ Å. $\omega_0=-0.039$ and $k_F=0.217$ Å^{-1}.

pointing to a large effect of magnetic correlation in this situation.

The NRG method is a very capable tool for studying correlation effects in magnetic adsorbates on surfaces. The demonstrated favorable scaling of errors with Λ brings more realistic (multiorbital) models within the reach of modern computing facilities. The technique for calculating ground-state energies is very general and it can be, for example, applied to calculate the response of the system (expectation values and susceptibilities) with respect to arbitrary perturbations.

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