obtained by subtracting from $S_i(nt_0)$ a smooth fit to $S_i(nt_0)$ and normalizing.

12. The power spectrum for the i^{th} sweep,

$$P_i(\nu) = |\Sigma_n \exp(i2\pi\nu n t_0) S_i(n t_0)|^2$$

was computed for frequencies between 5×10^{10} and 20×10^{10} Hz. Frequencies below this range were dominated by the overall trace shape, whereas those above require too good a beam focus to observe a signal. Each spectrum was normalized by its frequency average to form $I_i(\nu) = P_i(\nu)/\langle P_i(\nu)\rangle_\nu$. After $I_i(\nu)$ was computed for a series of sweeps, an average normalized power spectrum was computed, and this was used to calculate $M_i(\nu) = I_i(\nu)/\langle I_i(\nu)\rangle_i$, the individual sweep power spectrum normalized by the average power spectrum.
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Effective Coupling in Biological Electron Transfer: Exponential or Complex Distance Dependence?

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Calculations for a simple model electron transfer system and tuna cytochrome c demonstrate a dichotomy in the distance dependence of the effective coupling. In one regime, the effective coupling varies exponentially with distance and depends primarily on the average properties of the bridging material; in the other regime, the effective coupling has a complex distance dependence and is more sensitive to the details of the bridging material. Experiments and theory indicate that both regimes may occur in biological systems, providing a perspective on a recent controversy over the nature of the distance dependence.

Electron transfer is fundamental to a wide range of important biological processes, including respiration and photosynthesis (*1*). Recent experimental advances, such as structural data for relevant proteins (*2*), provide a basis for meaningful theoretical approaches to the transfer rate. From analysis of biological electron transfer systems and model proteins, a controversy has arisen concerning the dependence of the electronic coupling on the distance between the donor and the acceptor (*3*). It has been suggested both that there is a universal exponential dependence on the distance (*4*) and that the distance dependence is a complex function of the intervening material (*5*). These suggestions are not mutually exclusive. Depending on the energy difference between the bridge orbitals and the donor-acceptor orbitals, the electronic coupling can vary exponentially with distance or have a more complex behavior. The present treatment is based on the inverse matrix technique (*6*) for calculating the electronic coupling that includes all paths between the donor and acceptor. We apply the approach first to a one-dimensional (1D) (single-pathway) model and then to a calculation including all possible pathways between the heme and arbitrarily located acceptors in tuna cytochrome c (*7*).

The rate k for the long-distance, nonadiabatic electron transfer reactions occurring in proteins is usually assumed to be given by (*8*)

$$k = \frac{2\pi}{\hbar} |H_{\rm DA}|^2 ({\rm F.C.}) \qquad (1)$$

where $\hbar$ is Planck's constant divided by 2π. Electronic degrees of freedom determine the effective coupling ($H_{\rm DA}$), and nuclear degrees of freedom determine the Franck-Condon factor (F.C.). The effective coupling is explicitly dependent on the tunneling energy E (*6*), as is clear from the definition for $H_{\rm DA}$ in the one-electron approximation (*9*), which is given by

$$H_{\rm DA} = -\sum_{ij} \beta_{{\rm D}i} G_{ij}(E) \beta_{j{\rm A}} \qquad (2)$$

Here, $G(E) = (H_{\rm bridge} - E)^{-1}$ is the Green's function (*10*) for the bridge Hamiltonian $H_{\rm bridge}$. The indices i and j run over all orbitals involved in the transfer process, and $\beta_{{\rm D}i}$ ($\beta_{i{\rm A}}$) represents the coupling of the ith orbital to the donor (acceptor). Widely used pathway models approximate Eq. 2 by calculating the Green's function to lowest order in perturbation theory (*10*). In the single-pathway model, only the term that makes the most significant contribution to the sum is retained. The inverse matrix technique is an alternative to the approximate pathway method (*6*). It exploits the ease of matrix inversion to compute the Green's function exactly, including all terms in the sum. Although the pathway method may provide qualitative insight, more accurate methods, such as full matrix diagonalization or the more powerful inverse matrix technique (*6, 11*), are often required to attain quantitative accuracy.

The behavior of the effective coupling $H_{\rm DA}$ is labeled "exponential" if it depends exponentially on the donor-acceptor distance, and "complex" if its distance dependence is not exponential and is sensitive to the material intervening between donor and acceptor. The correlation coefficient $\rho(r, \log H_{\rm DA})$ between the donor-acceptor distance r and $\log H_{\rm DA}$ characterizes the behavior (*12*). If the effective coupling is an exponentially decaying function of distance, $\rho = -1$. If ρ is significantly different from -1 (greater than -0.5, say), we label the system as "complex."

An analytically solvable model, which has served as the starting point for many investigations since McConnell's original analysis (*13*), illustrates the classification scheme. The model consists of a donor orbital and an acceptor orbital with tunneling energy E connected to opposite ends of a linear chain of identical bridging ligands (Fig. 1A). We assume one orbital of energy $E_{\rm b}$ per ligand and include only nearest-neighbor coupling with hopping matrix element β. The behavior of the effective coupling is determined by the dimensionless parameter α (*6*)

$$\alpha = \frac{E_{\rm b} - E}{2\beta} \qquad (3)$$

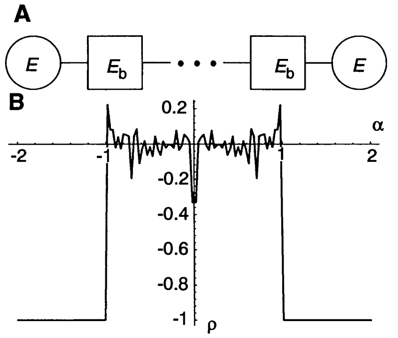

Fig. 1. (**A**) The McConnell model (*13*). Circles represent donor and acceptor orbitals, squares correspond to bridging orbitals, and lines represent coupling between orbitals with hopping matrix element β. The donor and acceptor terminate the chain and have energy E. The bridging orbitals have energy E_b. (**B**) Correlation coefficient ρ as a function of the dimensionless parameter α for the model 1D system. For a particular α, ρ is the correlation coefficient for the set $\{(2, \Delta_2), (3, \Delta_3), \ldots, (50, \Delta_{50})\}$, where Δ_n is the logarithm of the effective coupling for a bridge with n links. The effective coupling was computed analytically with a formula derived in (*6*).

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For $|\alpha| < 1$, the effective coupling oscillates as a function of the donor-acceptor distance (*6*); the behavior is complex. For $|\alpha| > 1$, the effective coupling decays exponentially with distance (*6*); the behavior is exponential. A plot of the correlation coefficient as a function of α (Fig. 1B) shows a sharp transition at $\alpha = \pm 1$ (*14*).

To explore the nature of the distance dependence in systems of biological interest, we treat a simple model for electron transfer in tuna cytochrome c. We assume that the heme iron is the donor and separately consider each of the 845 non-hydrogen protein atoms as possible acceptors; analogous calculations with the pathway model have been reported (*7*). The donor-acceptor distances are determined from the crystal structure (*15*), and the effective coupling is computed with the inverse matrix technique. We adopt a one-electron parameter set based on that of Beratan and Onuchic (*5, 16*) and vary the tunneling energy to analyze effective coupling behavior. This is analogous to varying α in the 1D model (see Eq. 3).

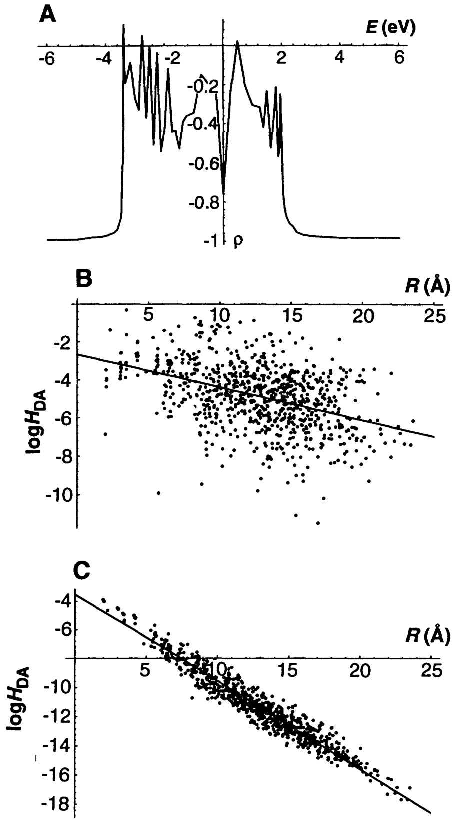

Fig. 2. (**A**) Correlation coefficient ρ as a function of the tunneling energy E for tuna cytochrome c. The coordinates for tuna cytochrome c were obtained from the Brookhaven Protein Data Bank. Hydrogen atoms were added on the basis of geometry by use of the program Quanta (Molecular Simulations, Inc.). Crystal waters were deleted. The effective single-electron Hamiltonian was computed with the parameters described in (*16*), and the inverse matrix technique was applied to obtain the effective coupling between the heme and the other 845 non-hydrogen atoms of the protein. (**B**) Logarithm of the effective coupling versus distance for tuna cytochrome c with $E = -2.0$ eV. Here $\rho = -0.42$, corresponding to complex behavior. (**C**) Logarithm of the effective coupling versus distance for tuna cytochrome c with $E = -4.0$ eV. Here $\rho = -0.97$, corresponding to exponential behavior.

For cytochrome c, sharp transitions of the correlation coefficient ρ as a function of tunneling energy, similar to those predicted analytically for the 1D model system, occur at about $E = -3.45$ and 2.03 eV for the present choice of parameters (Fig. 2A). Typical plots of the effective coupling versus distance for complex and exponential behavior appear in Fig. 2, B and C, respectively. Figure 2B is analogous to figure 1 in (*7*), which represents an equivalent calculation with a single-pathway approach (*17*). It is clear from Fig. 2B that there is a wide variation in $\log H_{DA}$ at a given distance. This variation demonstrates that the effective coupling is sensitive to the intervening material in the complex regime. The contrasting, essentially exponential variation of H_{DA} is evident in Fig. 2C.

For the 1D model, the minimum and maximum eigenvalues for the bridge Hamiltonian are $\pm 2\beta$. When the magnitude of the donor-bridge energy difference exceeds 2β, the effective coupling is exponential, and when the donor-bridge energy difference is less than 2β, the effective coupling is complex. Thus, the minimum and maximum values of the bridge eigenvalues define the transition between exponential and complex behavior. One reaches the same conclusion by computing the spectrum for cytochrome c, where the minimum and maximum eigenvalues [with use of the single-orbital parameter set determined as in (*16*)] are -3.446 and 2.028 eV, respectively; these values correspond exactly to the edges of the transition (Fig. 2A). Indeed, our results are consistent with notions derived from band structure in crystals (*10*), for which it has been shown that the off-diagonal matrix elements of the Green's function at energies not within a band decay exponentially with distance.

The parameter that controls the rate of exponential decay, generally denoted β (*4*) (not to be confused with the β in Hückel theory, used in Eq. 3 and elsewhere), depends sensitively on the tunneling energy. An explicit analytic relationship can be derived for the 1D model (*6*). For tuna cytochrome c, the numerical calculations indicate that Dutton's value of $\beta \sim 1.4$ Å^{-1} (*4*) corresponds to a difference between the tunneling energy and a typical bridge energy on the order of 2 to 5 eV. These values are clearly in the exponential regime. For values of the tunneling energy in the complex regime, the effective coupling may stay constant or even increase with increasing donor-acceptor distance; thus, the exponential decay parameter β is not rigorously defined. Nevertheless, almost all experimental studies of electron transfer report a value for β; small values (less than 1 Å^{-1}) may indicate complex behavior. Recent experiments on viologen-quinone molecules (*18*), myoglobin (*5*), and cytochrome c (*19*) are possible examples.

The tunneling energy is an essential parameter in determining the nature of the distance dependence. Unfortunately, the tunneling energy is difficult to determine quantitatively because it is sensitive to solvation effects. In the Hückel model, the energies depend on the ionization energies, and gas phase values can be obtained (*20*). In biological systems, however, both water and the surrounding protein act as "solvent" for the donor and acceptor moieties (*21*), as well as for the bridge elements. Although solvent effects complicate theoretical analysis, it may be possible to adjust the relevant energies experimentally by altering the molecule (point mutations) or applying external electric fields. Such experiments would provide information that could help determine which regime is applicable for a given system.

The present analysis provides a possible resolution to the controversy mentioned in the introduction. On one side of the debate are Onuchic, Beratan, Gray, and co-workers (*5*), who present theory and experiments on modified cytochromes showing that H_{DA} is sensitive to the bridging material. On the other side of the debate is Dutton's group (*4*), which finds that H_{DA} is determined by an exponential function of the donor-acceptor distance. It is possible that the behavior considered by the two groups corresponds to the different regimes described here. This is made plausible by a recent Hückel treatment of ruthenated myoglobin, where Siddharth and Marcus (*22*) suggest a 0.67-eV difference between the tunneling energy and typical bridge energies. Such a small energy difference corresponds to the complex distance dependence, which is found both in calculations and in experiments (*19*). It is interesting to note that in the exponential regime, the effective coupling depends only weakly on the details of the bridging material; so by operating in this regime, nature builds in tolerance against point mutations and other perturbations (*6*).

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12. The correlation coefficient of two random variables X and Y is (*23*)

$$\rho(x,y) = \frac{E(XY) - E(X)E(Y)}{\sigma_x \sigma_y} \qquad (4)$$

where $E(Z)$ is the expectation value of the random variable Z, and σ_z^2 is its variance. The correlation coefficient is bounded: $|\rho(X,Y)| \leq 1$. The equality holds if and only if Y depends linearly on X. Indeed, $Y = mX + b$ implies $\rho(X,Y) = m/|m|$, so that the sign of ρ agrees with the sign of the slope. If X and Y are uncorrelated, $\rho(X,Y) = 0$.
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14. In (*6*), we showed that the effective coupling for the 1D model decays monotonically for $|\alpha| > 1$ and exponentially only for $|\alpha| >> 1$. The subtle distinction between rapid monotonic decay and pure exponential decay is revealed in the present formalism by values of the correlation coefficient that approach, but never exactly equal, −1. The 1D results imply that as $|\alpha|$ becomes large, the correlation coefficient becomes arbitrarily close to −1, and this is confirmed by our calculations for cytochrome c. We call all behavior with $|\alpha| > 1$ exponential because in applications, it appears essentially exponential.
15. Coordinates were obtained from the file pdb5cyt.ent in the Brookhaven Protein Data Bank; T. Takano and R. E. Dickerson, *J. Mol. Biol.* **153**, 95 (1981).
16. It is difficult to develop a bridge Hamiltonian that is an exact translation of the Onuchic and Beratan "decay-per-bond" strategy. We use the definition in (*24*), where Onuchic and Beratan define [see table 1 in (*24*)] the site energy (diagonal matrix element) for all atoms in the molecule to be 0 (there is one orbital per site), the bonded atom hopping matrix element (β in Hückel theory) to be −0.881 eV, and the tunneling energy to be E = 2.0 eV; in the present work, we treat the tunneling energy as an adjustable parameter. To obtain the distance dependence of β for nonbonded atoms, we adapt an expression from (*5*)

$$\beta_{\text{nonbonded}}(r) = \lambda e^{-1\ 7(r-1\ 4)}$$

where r is the interatomic distance measured in angstroms. The prefactor λ is fixed by the requirement that $\beta(r_{CC}) = \beta_0/2$, where r_{CC} = 1.54 Å is the carbon-carbon bond length and β_0 = −0.881 eV is the bonded-atom hopping matrix element. Because the interaction between atoms separated by more than 8 Å is small, it is neglected.
17. Although Beratan and Onuchic write the effective coupling as an exponentially decreasing product, they find significant dependence on the chosen path. This may partially be a result of topological effects, but calculations that include all pathways between donor and acceptor indicate that single-pathway calculations overestimate fluctuations in the effective coupling at a given distance (*11*).
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Growth of High Aspect Ratio Nanometer-Scale Magnets with Chemical Vapor Deposition and Scanning Tunneling Microscopy

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A combination of chemical vapor deposition and scanning tunneling microscopy techniques have been used to produce nanometer-scale, iron-containing deposits with high aspect ratios from an iron pentacarbonyl precursor both on a substrate and on the tunneling tip itself. The structure and composition of the resulting nanodeposits were determined by transmission electron microscopy and high spatial resolution Auger electron spectroscopy. Either polycrystalline, relatively pure, body-centered-cubic iron or disordered carbon-rich material can be deposited, depending on the bias conditions of the tip sample junction and the precursor pressure. Two mechanisms of decomposition are inferred from the growth phenomenology.

The ability to control matter on decreasing length scales is expected to lead to significant scientific and technological advances. The scanning tunneling microscope (STM) offers the ultimate spatial resolution possible—manipulating materials down to the atomic level (*1*). For example, single atoms have been positioned on specific metal and semiconductor surfaces (*2–4*). The creation of interesting nanostructures requires the further ability to deposit a variety of different materials on substrates and to create clusters of atoms. Combining chemical vapor deposition (CVD) techniques with the STM offers great promise in this regard. Metal organic precursors are commercially available for many elements because of their widespread use in thin film technology (*5*). Furthermore, the local interactions present in an STM have already proved capable, in initial investigations (*6–10*), of decomposing certain precursors to leave behind metallic deposits. An additional and important challenge in such growth studies is knowing the nature of the resulting material. In general, it is difficult to characterize STM deposits by other microscopic or analytical techniques because of the small quantity of matter present (*11*). Although STM images provide an idea of the topology of small structures, it is not possible to discern their composition or crystalline phase.

We present here the results of an investigation of the growth of nanometer-scale iron deposits with a combination of CVD and STM techniques. In this study we were able to deduce the crystalline phase and composition of an STM deposit using transmission electron microscopy (TEM) and high-resolution Auger electron spectroscopy (AES). This leads to an understanding of the growth phenomenology and control of the resulting materials structure, composition, and shape on a nanometer scale. Specifically, we can control depositions on either the substrate or the tip by varying the growth conditions. We demonstrate the ability to produce high aspect ratio iron filaments with diameters less than 10 nm and aspect ratios greater than 80. Furthermore, by varying the bias conditions and precursor pressure we can form either amorphous or polycrystalline material. Filaments can be directly deposited on the apex of a silicon tip, which is part of a microfabricated silicon cantilever used in scanning force microscopy. Such nanodeposits will therefore find use in a variety of scanning probe microscopy experiments and are expected to extend the spatial resolution of these techniques.

We have used a modified commercial STM (*12*) in an ultrahigh vacuum (UHV) chamber (5 × 10^{-10} torr) designed to handle reactive gases over a wide range of

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