Ab-Initio Calculations of Materials Properties

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Introduction

Predicting and understanding the properties and behavior of real materials systems is of great importance both from technological and academic points of view. The theoretical problems associated with these systems are, of course, quite complex. However, we are currently at the forefront of beginning to overcome many of these problems.

Our research is devoted to creating a realistic microscopic quantum mechanical description of the properties of real material systems. In the past, theoretical attempts to deduce microscopic electronic and geometric structure have been generally based on optimizing a geometry to fit known experimental data. Our approach is more fundamental: predicting geometric, electronic, and dynamical structure, *ab-initio* — that is, given *only* the atomic numbers of the constituent atoms as experimental input. Briefly, our method makes it possible to accurately and efficiently calculate the total energy of a solid by the use of density functional theory, pseudopotential theory and a conjugate gradients iterative minimization technique for relaxing the electronic and nuclear coordinates. *Ab-initio* investigations are invaluable because they make possible theoretical calculations or simulations that can stand on their own. They may complement experimental observations but need not be guided by experimental *interpretations*. Our objective is to obtain a fundamental, microscopic understanding of various physical and chemical phenomena of real materials systems.

1. Silicon Surface Dimers and Physical Computing

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Because current bulk semiconductor-based designs are incapable of miniaturization past a closely approaching limit, we must look to different physical systems capable of logic operations as replacements. Research in this area [1-4] has focused on molecular electronics, cellular automata, nanotubes, and DNA. In choosing new avenues to explore, it would be helpful to have a guiding principle and general mechanism for information processing. In other words, we would like to search not only for specific new physical systems, but an entirely new paradigm for logic operations evident in a wide range of physical systems. Once we have identified which ones satisfy the requirements of the paradigm, technology can choose for us which system is most likely to succeed in practice.

In this work we have explored a new kind of information-processing paradigm which utilizes a class of inherently bistable systems. The bistability persists regardless of the inputs to the logic gate; a system parameter must be cycled to force the computation. By combining ab-initio studies with a simple analytic model of the Si surface system, we can analyze the parameterized motion of the fixed points (which represent the distinct digital states) in a bifurcation diagram. The

analysis shows that the effect of forcing the system past 'catastrophic points,' where one of these fixed points disappears, can be interpreted as a NOR universal logic gate.

We have recently shown, using density functional theory (DFT) calculations of total energy, that the system of three colinear buckled Si(100) surface dimers and an asymmetrically placed tungsten (W) scanning tip can be used to produce a NOR logic gate under proper adiabatic variation of tip position [5]. The two dimers on the side are inputs to the gate and the center is the output. The tip lowering and raising cycle forces the output dimer to a state determined by the inputs in the case that they are in the same state, or to a state determined by the tip asymmetry in the case that they are different. The important insight, and the point of this work, is that the mechanism for logic processing here is not necessarily unique to this system. In fact, the general features responsible may show themselves in a possibly wide and varying class of phenomena. We here attempt to outline the requirements for such an equivalent system.

We would like to analyze the motion of the fixed points (the states called '0' and '1') of the dimer potential under variation of the system parameters, in order to generalize the requirements for a class of similar systems. However, to do so by dense calculation of total energy with DFT would be prohibitively expensive. Therefore, we have modeled the dimer potential by a straightforward analytic expression that retains its important features.

The Si(100) dimer buckles because, after the surface reconstructs, there are only enough electrons to form one set of sp^3 (tetrahedral) hybridized orbitals. The remaining dimer atom, electron deficient, can only form sp^2 (planar) orbitals. The planar configuration of the latter atom forces it lower than the former, with respect to the bulk. Thus, the dimer buckling is directly controlled by the location of one electron orbital that can move from one dimer atom to the other, flipping the dimer.

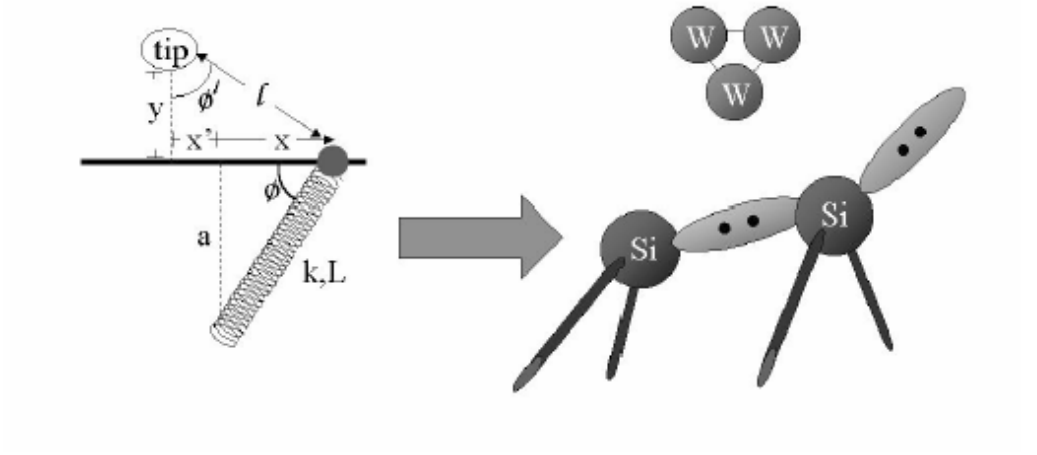

Figure 1. Right: the mechanical analog to Si(100) surface dimers we analyse, with appropriate variables labeled. Left: a schematic of a buckled dimer and tungsten scanning probe system, with filled electron orbitals shown as ovals with two dots.

A model to predict the dimer buckling orientation, therefore, can focus on the equilibrium positions of the electron potential (in the semiclassical sense). This potential is formed from the sum of the local interatomic potentials from the dimer atoms themselves, the bulk Si, the nearby dimers on the surface, and a weakly interacting W tip.

Our model for the dimer is based on a purely mechanical bistable system [6]. The electron orbital is modeled by a bead which is constrained to move on a wire between the dimer atoms, and is held by a fixed, pivoted spring of relaxed length *L* and spring constant *k*. See Fig. 1. If the spring is compressed when *x=0*, two equivalent stable minima will appear for *x<0* and *x>0*. However, the dimer energy minima are not equivalent. This evident asymmetry is a result of the influence of the orientation of nearby dimers. The potential due to this interaction may be quite complicated owing to the fact that it is coupled through intermediate lattice atoms. However, we can model it sufficiently by retaining just the first order term of an expansion, which is assumed to be the dominating term. (The mechanical analog to this interaction is a constant force like gravity, which becomes important if the wire is at an angle from horizontal.) This parameter may be determined by fitting the potential to that obtained using DFT calculations. The remaining interaction is from the W tip. From DFT calculations of total energy we deduce that the interaction is attractive. The W tip atom forms a partial bond with the Si atoms, by 'sharing' valence electrons. We take our basic model from the Morse molecular potential [7].

To illustrate information processing with this system, refer to Fig. 2. Here we have numerically integrated our force model with Gaussian quadrature to obtain a potential energy curve as a function of electron orbital position, u. The parameters are been chosen such that the energy of this mechanical system as a function of u has similar features as the energy of the Si dimer system as a function of dimer angle.

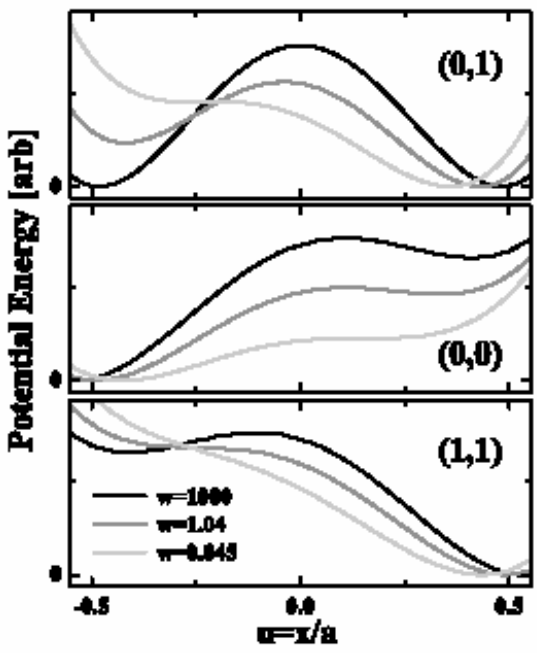

Figure 2. The potential energy curves for inputs A and B =(0,1) (top), (0,0) (middle), and (1,1) (bottom) for the Si(100) dimer model. At large tip distance w, the system is always bistable. Past a critical value, however, one stable minimum disappears.

Interpreting the minima of each curve, at constant w, as distinct states, we see that as the tip is lowered, (parameter w is decreased) the potentials are reduced to one unique stable state. Raising the tip completes a cycle. Regardless of which state the system started in at large w, the final state will be the one which survived the 'catastrophe' when the other disappeared.

Let us now analyze the trajectories of these critical points as the tip height parameter is varied. See, for example, Fig. 3 (top), corresponding to (inputA, inputB)=(0,1). Here we have numerically solved for the roots of our Force model, using the Van Wijngaarden-Dekker-Brent algorithm. The parameters are the same as above, with h=0. We see that reducing the tip height parameter adiabatically forces the system past a catastrophe near w=0.85 where one stable minimum and the unstable maximum annihilate each other. Starting on this stable branch, '1', at large w, the system will follow the path towards this point. Past this cusp-type catastrophe, only one stable state remains, '0'. The system quickly relaxes to this new branch.

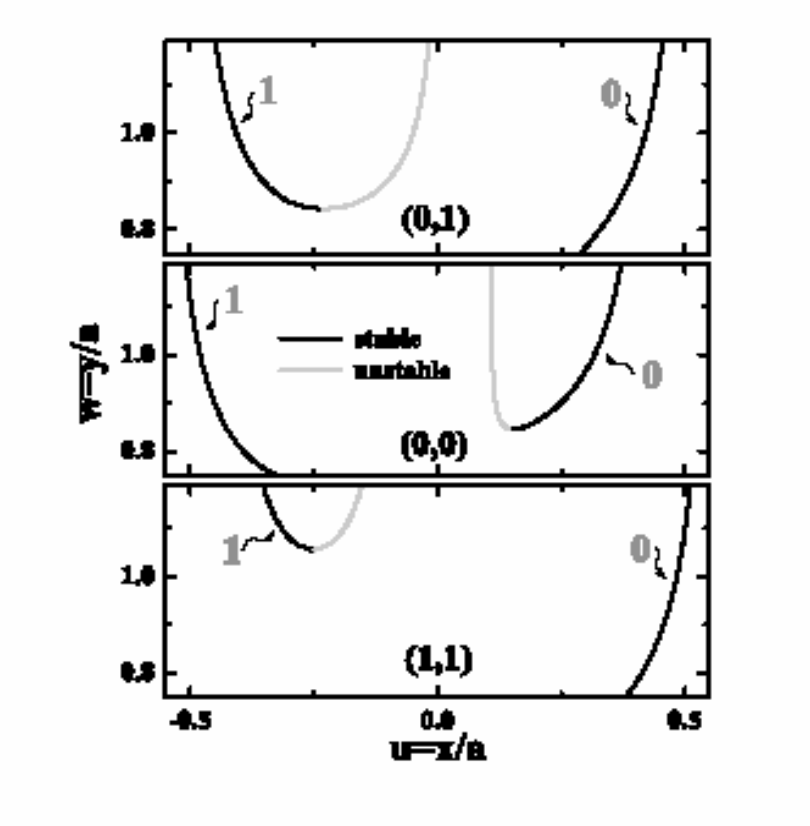

Figure 3. (Top): Bifurcation diagrams corresponding to the potential energy curves in Fig 2. As w adiabatically decreases, a stable minimum and unstable maximum annihilate each other, leaving only one fixed point. When w increases, the system stays on that stable branch. This hysteresis is determined by the inputs in a way which is equivalent to a NOR logic gate.

When the cycle reverses its path, there is no way for the system to deviate from this locus of connected critical points. At the end of the cycle, the system does not return to its starting point, but remains in the other stable minimum. This hysteresis is responsible for information processing; the result of the logic operation with inputs '0' and '1' is '0'. Comparison of Figs 3 (top), (middle), and (bottom) show that the same tip lowering cycle results in a final state determined solely by the inputs. The association between the input and output states for all possibilities is analogous to the logical NOR gate. (By switching the definition of '0' and '1', this gate becomes a NAND gate.) The NOR gate is a universal logic gate, which can be used to form any other logic gate.

Let us now conclude with a discussion of the salient features of this model. Clearly we require a bistable system with an "anti-ferromagnetic"-like interaction with the inputs (in this case Si dimers). A ferromagnetic interaction would result in the non-inverting (and thus non-universal) logic gates AND or OR.} interaction. We also require a mechanism for destroying the bistability of the output without removing the asymmetry (W tip). However, the influence of the inputs are additive, so when the inputs are opposite ('(0,1)'), we need a residual asymmetry to pin the system to a definite state. In the model above, this asymmety is provided by the shift of the tip lowering axis from the center of the wire. These requirements result in a bifurcation diagram with the general topology of connected minima shown in Fig. 3.

References

1. J. Chen, M.A. Reed, A.M. Rawlett, and J.M Tour, *Science* **286** 1550 (1999).
2. G.L. Snider, *J. Appl. Phys.* **85**, 4283 (1999); R. P. Cowburn and M. E. Welland, *Science* **287**, 5457 (2000).
3. R.J. Lipton, *Science*, **268**, 542 (1995).
4. Y. Huang, X. Duan, Y. Cui, L. Lauhon, K. Kim, and C. M. Lieber, *Science* **294** 1313 (2001).
5. Appelbaum, T. Wang, S. Fan, J.D. Joannopoulos, V. Narayanamurti, *Nanotechnology* **12**, 391 (2001).
6. S.H. Strogatz, *Nonlinear Dynamics and Chaos*, Westview Press, Cambridge, (2000).
7. P. M. Morse, *Phys. Rev. B***34**, 57 (1929).

Publications

Journal Articles Published

C. Luo, S. Johnson, J. Joannopoulos, and J. Pendry, "All-angle Negative Refraction without Negative Effective Index," *Phys. Rev. B***65** (RC), 201104 (2002).

S. Hart, G. Maskaly, B. Temelkuran, P. Prideaux, J. Joannopoulos, and Y. Fink, "External Reflection from Omnidirectional Dielectric Mirror Fibers," *Science* **296**, 510 (2002).

M. Watts, S. Johnson, H. Haus, and J. Joannopoulos, "Electromagnetic Cavity with Arbitrary Q and Small Modal Volume without a Complete Photonic Bandgap," *Optics Letters* **27**, 1785 (2002).

Y. Yi, P. Bermel, K. Wada, X. Duan, J. Joannopoulos, and L. Kimerling, "Si-based Low-voltage Tunable Omnidiectional Reflecting Photonic Bandgap Materials with Large Air Defects," *Appl. Phys. Lett*. **81**, 4112 (2002).

M. Soljacic, S. Johnson, S. Fan, M. Ibanescu, E. Ippen, and J. Joannopoulos, "Photonic Crystal Slow-light Enhancement of Nonlinear Phase Sensitivity," *J. Opt. Soc. Am. B***19**, 2052 (2002).

C. Luo, S. Johnson, and J. Joannopoulos, "All-angle Negative Refraction in a 3D Periodic Photonic Crystal," *Appl. Phys. Lett*. **81**, 2352 (2002).

B. Temelkuran, S. Hart, G. Benoit, J. Joannopoulos, and Y. Fink, "Wavelength-scalable Hollow Optical Fibers with Large Photonic Bandgaps for CO_2 Laser Transmission," *Nature* **420**, 650 (2002).

S. Fan and J. Joannopoulos, "Analysis of Guided Resonances in Photonic Crystal Slabs," *Phys. Rev. B***65**, 235112 (2002).

S. Johnson, M. Ibanescu, M. Skorobogatiy, O. Weisberg, J. Joannopoulos, and Y. Fink, "Perturbation Theory for Maxwell's Equations with Shifting Material Boundaries," *Phys. Rev. E***65**, 066611 (2002).

M. Soljacic, M. Ibanescu, S. Johnson, Y. Fink, and J. Joannopoulos, "Optimal Bistable Switching in Nonlinear Photonic Crystals," *Phys. Rev. E***66**, 055601 (RC) (2002).