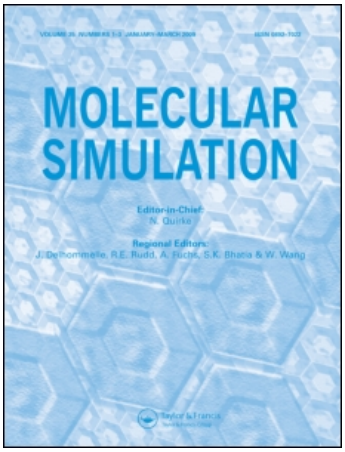

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First Principles Methods *versus* (Semi) Empirical Methods: Modeling the Hierarchy of Length Scales in Material Systems

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FIRST PRINCIPLES METHODS *VERSUS* (SEMI) EMPIRICAL METHODS: MODELING THE HIERARCHY OF LENGTH SCALES IN MATERIAL SYSTEMS

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It is argued here that first principles methods and (semi-)empirical methods are *both* essential in studying the hierarchy of length scales that are pertinent to solid state systems. Accurate quantum mechanical methods based on density functional theory are pertinent to small systems comprising a few thousand atoms. It is more appropriate to use accurate effective Hamiltonians for larger system sizes for reasons of computational efficiency *and* because the microscopic details are less important. This paper emphasizes the need for deriving a hierarchy of methods from a fundamental theory that are applicable to varying length scales in solid state systems.

Keywords: First principles methods; semi-empirical methods; length scales

I. INTRODUCTION

With the advent of modern computers there appears to be a belief that with sufficient computer power, any problem in materials science can be understood with sufficient accuracy. The rationale is that today, since we have the theoretical and computational machinery in place to understand systems of a few hundred atoms very accurately, it must surely only depend on the access to more computer resources and power for one to be able to investigate systems of the mesoscopic or microstructural length scales with the *same* degree of accuracy. It is often said that the understanding of real material systems, with all the complexity of surface effects, defects, impurities, including varying conditions of alloying, temperature, pressure, *etc.*, *etc.* is only a 'big' computer away.

Unfortunately, for too long now have industrialists stumbled across workable materials solutions to industrial problems in an *ad hoc* fashion and without the support of physicists or material scientists. These scientists have usually only arrived at the scene after the fact and have not necessarily contributed to materials development in any meaningful way – here, it is mainly the theoretical and computational scientists that are being addressed, particularly the first principles total energy physicist. In my view despite our claims to be working on industrially important problems, we are not working synchronously with industry – often being totally out of step, addressing irrelevant aspects of otherwise industrially important systems, and often a little too late.

Density functional theory [1, 2] has proved to be highly accurate in predicting physical, mechanical, electronic and optical properties of systems, although many of the applications have been to reasonably ideal systems comprising a few hundred atoms. New algorithms are being developed, and exciting new computing architectures are being employed to extract maximum mileage from density functional theory, and this will remain an exciting field of research for some time to come.

An important point of this discussion is that if computational material scientists are to make a meaningful contribution to industrial needs, then we need to form partnerships that are highly focussed on solving real materials problems. We need to use all tools available to accomplish this task, and the first principles total energy scheme is just one type of tool at our disposal. The purists' view to insist on only using *ab initio* methods is short-sighted which further delays deriving solutions for real needs.

The resurgent interest in magnesium-based alloys is a case in point. Due to the high legislative constraints placed by the US government on the emissions of gasoline-driven automobiles, with the requirement that there be zero-emission vehicles commercially available early in the next century, the auto manufacturers have begun to invest heavily in research into light metal alloys, with Mg-based materials having particular advantages. Much of this research, of course, is experimental. Computational material scientists have the tools to tackle the problems of industry, but they have not entered this field with much enthusiasm. Perhaps this is due, in part, to the fact that the highly accurate quantum mechanical calculations are not capable of addressing the tonnage sizes that are needed on the shop floor? Improving algorithms and more powerful computers are not going to help us transcend these length scales in the near future, but more importantly, this is not necessary – we should not wait for the field of quantum mechanical computational material science to evolve to this extent before we

begin to seriously look at industrial type of materials problems. At this time we *do* have the necessary ingredients to establish a stronger bond with industry.

The *ab initio* scientists, the empirical scientists, the chemists, the material scientists, the experimentalists and the industrialists must begin to work closely with each other, each drawing on the other's strengths and experiences to enable a more serious resolution of materials problems relevant to the real world. We must be able to merge from one activity into another, and a blurring of the lines separating each of these activities is absolutely vital. This is multidisciplinary research, and yet to a nonspecialist the differences between these activities must seem minute – and indeed they are!

II. VARYING LENGTH SCALES

In terms of computational materials science, the challenge is to develop methods that will enable one to telescope into different length scales that are pertinent to different phenomena in the solid. We need to be able to move continuously from the first principles quantum mechanical picture to the semi-empirical models that are more apt at the millimetre microstructural level which is the world of material science. At this level it could be argued that the graininess of quantum mechanics is less important than at the electronic level, but clearly more important than at the Newtonian macroscopic level. The merging of quantum mechanics into classical mechanics is a profound issue, but here a practical scheme is being sought whereby one can move smoothly from one world into another.

Figure 1 [3] describes the hierarchy of disciplines based on varying length scales. The quantum mechanical studies of systems including the electronic degrees of freedom is at the fundamental level, and because of the high computational effort involved in studying such systems it is only possible at present to study systems of order 1000 atoms. Improving algorithms and more powerful computers should increase this number to tens of thousands of atoms for routine calculations in the near future.

The atomistic picture involves treating the ions as spheres interacting *via* some potential. Pair potentials are usually not adequate for treating most systems, and it has been found that many-body corrections are important for better quantitative agreement with experiment. Many of the parameterized empirical potentials suffer from problems of low transferability, and so there is a need for a more systematic means of improving these schemes. The

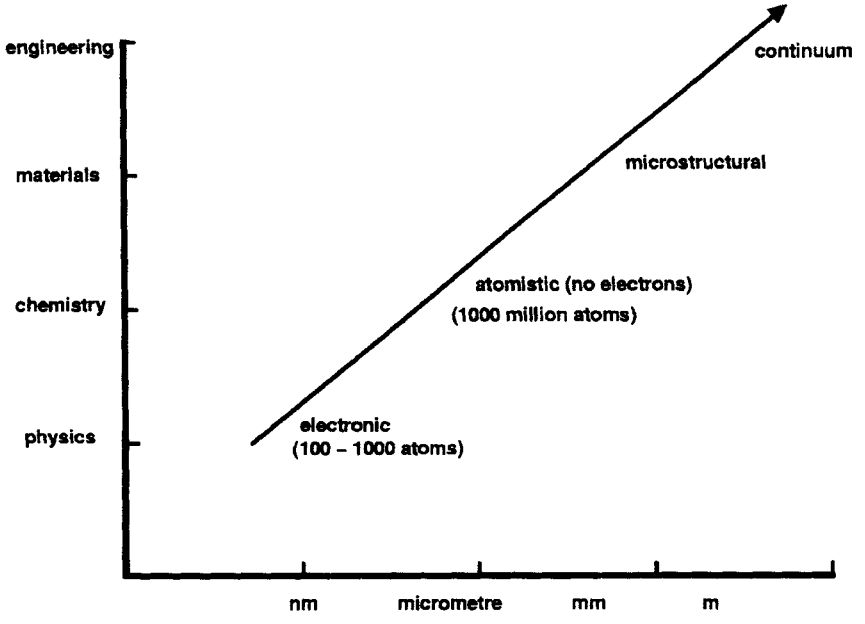

FIGURE 1 The hierarchy of length scales in material systems.

atomistic view enables one to look at larger system sizes of order 1000 million atoms. Defect structures with long range effective interactions such as dislocations or systems with slowly decaying Friedel oscillations can be more accurately studied in this regime. Also, finite size effects at phase transitions are diminished in these larger system sizes.

The microstructural view of matter at the millimetre length scale signals the onset of materials science, involving elastic constants and stress-strain relationships, and this merges into the continuum which is a classical picture of solids based on the constitutive relations involving macroscopic electric and magnetic fields. The computational methods for working in these regimes, such as finite element calculations, are simpler and so it is efficient to consider macroscopic system sizes.

It would be ideal to be able to transcend each of these length scales continuously. Historically, in the study of solids, each discipline of physics, chemistry, material science and engineering evolved independently, and the focus of each field was narrow and essentially nonoverlapping. Today, however, the boundaries of each of these disciplines has been pushed sufficiently that interdisciplinary work is now imperative. The formal interconnection between different models used in the different disciplines is

difficult to make because of history, but yet the connections are implicity there. It would be satisfying to develop a hierarchy of approximations from the fundamental quantum mechanical method that will give rise to a hierarchy of models that would be applicable to the hierarchy of length scales in solids. First principles methods and empirical modeling are clearly *both* essential for the computational studies of material systems.

If the nuclei are treated as point particles, and when one assumes the Born-Oppenheimer view that the electrons are in the ground state for the instantaneous positions of the ions, then density functional theory within the local density approximation [4] (including local spin or gradient corrections) is a working quantum mechanical scheme for many types of systems. Here, we are excluding systems that exhibit exotic electronic behaviour such as superconductivity where correlation effects are important, although there are systematic means of correcting for many of these effects.

The empirical and semiempirical methods invariably omit the electronic degrees of freedom, and the task then is to find an effective Hamiltonian for the system under investigation. A good deal of intuition is required to write down the details of the model, and parameters are usually fitted to experiment or to other theoretical calculations. The problem often arises in the universality or the transferability of the parameters: models that are fitted to bulk properties are often not suitable for describing surface effects and *vice versa*. Atomic parameters fixed in one chemical environment might not be applicable or accurate in another chemical environment. Also, when the model fails there often is no clear means of correcting for the deficiency – just simply adding on another parameter may not be meaningful and does not necessarily enhance the understanding of the physical system.

This calls for a more systematic approach to deriving semi-empirical models from the more accurate quantum mechanical method. A good deal of intuition is still required, and the aim is to develop a hierarchy of theories or models with each level of approximation that would be applicable to varying length scales.

III. PRACTICAL NOTIONS

It is not the aim of this paper to provide an exhaustive list of the many creative practical notions that exist that systematically address the issue of transcending length scales in solids starting from the fundamental quantum mechanical picture. The author has chosen instead to focus on a few points

that demonstrate these notions with the assertion that a lot more needs to be done in this field.

Kohn's [5] concept of 'near-sightedness' of solid state systems is an appropriate starting point. It is argued that even though quantum mechanics is nonlocal, in reality however, because of screening effects, an ion in a solid state environment has only a limited view of its surroundings. This justifies an approximate expansion for the density matrix in terms of localized Wannier-like functions where the expansion set size is independent of system size. For systems with a gap the density matrix is short-ranged with an exponential decay. This is the basis for some of the algorithms that solve the electronic structure problem with linear scaling [5].

Physically, this makes sense: When a long bar of copper has its tip broken, the remaining piece still remains bulk copper with essentially unchanged heat capacity, resistivity, bulk modulus, elastic constants, melting temperature, *etc.* Apart from the region closest to the break, the majority section of the copper bar has apparently not 'seen' the break, or been affected by it. Now, an accurate quantum mechanical calculation would need to take into account the changed potential interactions and boundary conditions, and in principle all electronic and ionic interactions in the system are affected. In practice, since only the region closest to the break has experienced any appreciable change in its physical and possibly its chemical environment, it makes sense that only this region be modeled as a deviation from the original bulk region. And so may associate an integrating region about each ion which is its field of sight.

This view of solids is the basis of a number of algorithmic developments, and it gives credence to a number of models, such as the various augmented schemes, which take a localized view of matter, many of these schemes of which were borne out of computational expediency rather than physical argument.

The local energy density also takes a localized view of matter. Chetty and Martin [6] defined the energy density $\varepsilon(\mathbf{r})$ as

$$E_{\text{tot}} = \int_V d\mathbf{r}\, \varepsilon(\mathbf{r}), \tag{1}$$

where V is the volume of the entire system and E_{tot} is the total energy. Clearly $\varepsilon(\mathbf{r})$, being defined in terms of an integral equation, is nonunique. While E_{tot} is always well defined (since all gauge dependences integrate to zero over the entire volume of the system), it was demonstrated that the integral above could still makes sense when the region of integration v is

contained within the volume V. In the calculation of the energetics of GaAs surfaces it was shown that the appropriate integrating region was one that was bounded by bulk symmetry planes – the so-called symmetry adapted cells [7] – which gave rise to gauge-independent integrated physical results. So, in the absence of long-range electric fields, the energy density is a useful construct to derive local information within the field of view. A local energy, and its derivatives (local forces and stresses, *etc.*) give important ground state information such as equilibrium structure. Unfortunately, no algorithm has been devised to solve directly for the local energy density. Clearly, such a scheme will be very useful, and could be the basis for devising schemes for transcending length scales.

The Harris [8, 9] functional is a useful stepping stone to deriving approximate total energy methods. This functional is stationary at the ground state energy. It is a nonselconsistent scheme and it only needs an optimized input charge density [10]. Foulkes and Haydock [9] used the Harris functional to place on firmer theoretical footing the tight binding scheme. It is well known that the latter scheme is well suited to studying large system sizes because of the simplicity of the method. When the tight binding method fails, the Harris functional provides a clear means, in principle, of correcting for deficiencies because of the hierarchy of approximations.

It was recently shown that the Harris functional could also be used to derive an *ab initio* effective medium theory [11]. This provides the basis for explaining the successes of the semi-empirical effective medium theory [12], the embedded atom method [11] and a variety of other similar methods [11]. A crucial approximation called the 1-electron correction, which is related to the integrated local density of states function, must be improved to make this one of the more successful of the hierarchical methodologies.

Finally, in the recent modeling of stacking faults in magnesium [13], it was shown that highly detailed Brillouin zone integrations [14] were required to derive accurate total energies. This was needed because, firstly, the energies of these defects are small (of order tens of mev) and so an accurate calculation depends sensitively on the details of the sampling of the Brillouin zone and, secondly, because supercells of varying sizes were needed to construct the faults (the extrinsic fault necessarily has one additional atomic plane compared with the intrinsic fault). Because of the computational effort involved in considering hundreds of **k** points for the various stacking fault geometries, the work was performed on a massively parallel machine involving hundreds of node hours of computations. The highly accurate calculations enabled the construction of a successful bond orientation

scheme that was able to, firstly, reproduce all calculated results with mev accuracy and, secondly, predict the energies of totally new structures with the same degree of accuracy. Because of the short-range nature of the interactions the authors were able to consider systems of arbitrarily large sizes, and in particular they were able to perform a finite temperature extension including configurational entropy effects. There are many examples of this type of scheme: a highly accurate quantum mechanical calculation is the basis for constructing a model Hamiltonian which is then amenable to a finite temperature extension.

IV. FINAL REMARKS

We need more tangible model connections across the different length scales that are relevant to solid state systems. It is advocated that from the fundamental quantum mechanical picture we derive a hierarchy of models based on a hierarchy of approximations that will continuously transcend these different lengths. A lot of progress has been made and this remains an exciting field for future development. This field of research is crucial for a more serious resolution of real materials type problems – it is important that more accurate models be applied to the study of microstructural systems where, in the event of failure, there is a systematic means of upgrading the model by telescoping to a shorter length scale.

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