

# DERIVATION OF INTERATOMIC POTENTIALS BY INVERSION OF *AB INITIO* COHESIVE ENERGY CURVES

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## ABSTRACT

An analytic procedure for inverting *ab initio* cohesive energy vs. volume curves to obtain a parameter-free interatomic potential is presented. The procedure determines the radial functions in a cluster potential, assuming an angular dependence. The method is a nonlinear generalization of the *ab initio* pair potential formula of Carlsson, Gelatt and Ehrenreich to higher orders of cluster expansion [1]. We demonstrate our method by deriving an *ab initio* cluster potential for silicon with the Stillinger-Weber angular dependence [2]. A novel property of the potential is that bond-bending forces are not monotonic in the bond length, as is the case with most empirical potentials, but rather are peaked at the first neighbor distance. The validity of the inverted potential is discussed along with its use in the development of new interatomic potentials.

## INTRODUCTION

Classical interatomic potentials could play a crucial role in the study of complex materials phenomena through large-scale molecular dynamics simulations because they allow a much faster evaluation of energies and forces, compared to quantum mechanical methods. What is limiting the applicability of classical potentials is that typically, efficiency is attained at the cost of accuracy. For semiconductors like silicon, the prototypical covalent material for developing new potentials, the situation is particularly demanding because pair potentials, which work well for metals and ionic solids, are simply not adequate [3]. Theories that discuss the basic form of a cluster expansion for an empirical potential [3, 4] provide little guidance on the specific form of the potential: The form is usually an educated guess, motivated by physical intuition and containing a number of adjustable fitting parameters [5].

In this paper, we present a method for obtaining parameter-free classical potentials directly from first principles quantum mechanical energy calculations. A truncated cluster expansion for the cohesive energy of a crystal implies a functional relationship between the energy and various factors in the expansion. Inversion of this relationship leads to determination of the radial functions in the cluster expansion. For three-body and higher order terms, angular dependences must be assumed. Our method represents a generalization of the “*ab initio* pair potential” of Carlsson, Gelatt, and Ehrenreich (CGE in the following), originally applied to metals [1]. The inversion procedure provides theoretical insight to guide the development of new empirical potentials and may produce useful interatomic potentials for semiconductors without the arduous and uncontrolled process of fitting adjustable parameters.

## THEORY

We begin with a brief description of the inversion method. Consider an isotropic crystal structure defined by a set of atomic positions  $\{\vec{R}_i\}$  about a central atom located at the origin. Let  $r$  be the nearest neighbor distance, and group the atoms into shells of radius

$s_p r$  containing  $n_p$  atoms each. Number the shells so that  $s_1 < s_2 < s_3 < \dots$ . By construction  $s_1 = 1$ . Isotropic expansion and contraction of the crystal is described by varying  $r$  while keeping  $\{s_p\}$  and  $\{n_p\}$  constant. Assume first that the cohesive energy is completely described by a pair potential interaction,

$$E[\phi](r) = \sum_i \phi(R_i) = \sum_{p=1}^{\infty} n_p \phi(s_p r). \quad (1)$$

Then separate the first shell term from the sum in Eq.(1), and solve for  $\phi(r)$ ,

$$E(r) = n_1 \phi(r) + \sum_{p=2}^{\infty} n_p \phi(s_p r) \quad (2)$$

$$\phi(r) = \frac{1}{n_1} \left( E(r) - \sum_{p=2}^{\infty} n_p \phi(s_p r) \right). \quad (3)$$

Now view Eq.(3) as a recursion: by recursive substitution for  $\phi(r)$ , we obtain

$$\phi[E](r) = \frac{1}{n_1} E(r) - \sum_{p=2}^{\infty} \frac{n_p}{n_1^2} E(s_p r) + \sum_{p,q=2}^{\infty} \frac{n_p n_q}{n_1^3} E(s_p s_q r) - \dots, \quad (4)$$

which is identical to the expression obtained by CGE. The original derivation of the inversion formula by CGE relies on the linearity of  $E[\phi]$ , and thus cannot be generalized to higher orders of cluster expansion, in which products of radial functions appear [1]. All that is required for our derivation, however, is the ability to solve for  $\phi(r)$  in terms of  $\phi(s_p r)$  for  $p \geq 2$ , which permits a straightforward generalization to higher order terms.

Our approach reveals the mathematical structure of the CGE formula in a simple manner: the pair potential at  $r$  is chosen so that the first neighbor contribution to the cohesive energy,  $n_1 \phi(r)$ , provides exactly the energy left over from interactions with higher shells. A simple consequence of this observation is that, if  $\phi(r')$  is known for all  $r' > r$ , then Eq.(3) uniquely determines  $\phi(r)$ . This suggests an analytic procedure that does not involve an explicit formula like Eq.(4). Suppose that the potential has a cutoff distance  $a$  such that  $\phi(r) = 0$  for  $r > a$ . The pair potential can then be generated by solving for  $\phi(r)$  using Eq.(3) in order of decreasing  $r$  starting at the cutoff. The sums in the CGE formula are implicitly contained in the procedure. In addition to providing a simpler way to compute the potential, our procedure is crucial for nonlinear energy functionals in which it would be cumbersome even to write down the explicit formulae.

Now let us generalize of the procedure to the next order in the cluster expansion. Define the many-body component of the cohesive energy by subtracting off the pair contribution,

$$F_C(r) = E_C(r) - \sum_{p=1}^{\infty} n_p \phi(s_p r), \quad (5)$$

where  $C$  denotes the crystal structure. In the following derivation we must assume that  $F_C(r)$  is known, i.e. that  $\phi(r)$  can be determined, either directly or by inversion of  $E_{C_0}(r)$  for some  $C_0 \neq C$ . The latter case is possible only if the angular dependence in  $C_0$  makes the many-body terms vanish (as for example, in the diamond lattice for silicon empirical potentials [5]).

Although more complicated cluster potentials and cluster functionals can be accommodated, we will only consider separable three-body potentials of the form [2, 6],

$$F[g, h](r) = \sum_i \sum_{j>i} g(R_i) g(R_j) h(\theta_{ij}), \quad (6)$$

where  $\cos \theta_{ij} = \hat{R}_i \cdot \hat{R}_j$ . Assuming that we are given the angular dependence  $h(\theta)$ , then we can invert  $F[g]$  to obtain the radial function  $g(r)$  as follows: With  $A_p$  denoting the set of atoms in shell  $p$ , define,

$$\alpha_{pq} = \sum_{i \in A_p} \sum_{j \in A_q} h(\theta_{ij}), \quad (7)$$

where in the second sum, if  $p = q$ , then only  $j > i$  should be considered to avoid double counting a triplet of atoms. With these definitions, the many-body contribution to the cohesive energy becomes,

$$F(r) = \sum_{p=1}^{\infty} \sum_{q=p}^{\infty} \alpha_{pq} g(s_p r) g(s_q r). \quad (8)$$

Separate the terms involving only  $g(r)$ ,

$$\begin{aligned} F(r) &= \alpha_{11} g(r)^2 + \left[ \sum_{p=2}^{\infty} \alpha_{1p} g(s_p r) \right] g(r) + \left[ \sum_{p=2}^{\infty} \sum_{q=p}^{\infty} \alpha_{pq} g(s_p r) g(s_q r) \right] \\ &= \alpha_{11} g(r)^2 + \beta(r) g(r) + \gamma(r), \end{aligned} \quad (9)$$

where  $\beta(r)$  and  $\gamma(r)$  denote the corresponding terms in square brackets, giving

$$g(r) = \frac{-\beta(r) + \sqrt{\beta(r)^2 + 4\alpha_{11}(F(r) - \gamma(r))}}{2\alpha_{11}}. \quad (10)$$

We have chosen the positive root in the quadratic formula, because the many-body energy should be positive [3]. As before, the idea is to view Eq.(10) as a recursion, since  $g(r')$  appears in the expressions  $\beta(r)$  and  $\gamma(r)$ . An explicit formula could be obtained by recursive substitution, but it involves a complicated set of nested square roots. As in the pair potential case, it is much simpler to use the recursion directly in place of an explicit formula. The right hand side of Eq.(10) depends only on  $r'$  for  $r' > r$ , so we can solve for  $g(r)$  in order of decreasing radius starting at the cutoff distance.

## APPLICATION TO SILICON

To illustrate the inversion procedure, we have performed density functional calculations in the local density approximation (LDA) to obtain the cohesive energy vs. volume curves for silicon in the cubic diamond and  $\beta$ -tin structures. We use a plane wave basis with a 12 Ry cutoff and 512 points in the full Brillouin zone for reciprocal space integrations. The LDA data is shifted, by choosing the appropriate energy for an isolated atom, so that the equilibrium binding energy for the diamond structure is equal to the experimental value of -4.63 eV [5].

In order to invert the energy curves, an interpolant must be constructed so that the energy can be sampled at arbitrary volume (or, equivalently, at any first neighbor distance). Following CGE, we use rational interpolation in the region of calculated cohesive energy values and an exponential tail,  $a \exp(-br - cr^2)$ , for larger distances. The coefficients  $a$ ,  $b$  and  $c$  are chosen so that the interpolant is continuous with two continuous derivatives. Curve (i) of Fig. 1(a) shows the LDA data points for the diamond lattice with the interpolant.

For reasons discussed below, it is also instructive to consider a shorter cutoff for the potential, which, of course, implies the same cutoff for the energy. As an example, we choose the Stillinger-Weber (SW) cutoff distance  $a = 3.77118 \text{\AA}$ . Smooth cutoff of the energy at

$r = a$  is accomplished by multiplying the interpolated curve by the following function,

$$f(r) = \begin{cases} 1 & \text{if } x \leq 0 \\ \exp(\sigma) \exp\left(\frac{\sigma}{x^2-1}\right) & \text{if } 0 < x < 1 \\ 0 & \text{if } x \geq 1 \end{cases}, \quad (11)$$

where  $x = (r - (a - \delta))/\delta$ . This choice of cutoff function is continuous with all derivatives continuous, except at  $x = 0$  where only one derivative is continuous. It also has exactly the asymptotic behavior of the SW pair potential at the cutoff distance with the choice  $\sigma = 2\sigma_{SW}/\delta = 3.49183\text{\AA}$  [2]. The smoothing range  $\delta = 1.2\text{\AA}$  is chosen to allow for flexibility in cutting off the original curve while maintaining the exact energy values near the minimum in order to preserve important equilibrium properties (*e. g.* binding energy, lattice constant, and bulk modulus). The inversion procedure is implemented by starting at the cutoff, and solving for  $\phi(r)$  at equally spaced mesh points ( $\delta r = 0.011\text{\AA}$ ) using piecewise quadratic interpolation to evaluate  $\phi(r')$  for  $r' > r$ .

The pair potential is shown in Fig. 1(b) for energy curves (i) and (ii). The potential obtained from the energy curve before the cutoff is applied (i), the CGE potential, has long range. The equilibrium volume is set by a balance between a repulsive force among first neighbors and an attractive force among second and third neighbors. The situation is quite different, however, after the cutoff is applied (ii): In that case the potential is short-ranged with the equilibrium volume set by a zero force interaction with only the first neighbors.

The LDA data for  $\beta$ -tin is interpolated and is cutoff in a similar way as diamond. The many-body energy  $F(r)$  is computed using the inverted pair potential (ii). To ensure that  $F(r) > 0$  in the smoothing range, a larger value of  $\sigma$ , 4.15, is required. As an important example, we assume the widely-used Stillinger-Weber angular dependence [2],  $h(\theta) = \left(\cos(\theta) + \frac{1}{3}\right)^2$ , which vanishes at the tetrahedral angle, so that  $F(r) = 0$  for the diamond lattice (the  $C_0$  lattice introduced earlier). In order to get reasonably fast decay of  $g(r)$  at the cutoff,  $F(r)$  is multiplied by the same cutoff function as  $E(r)$ . This only affects energies in the original smoothing range and gives  $g(r)$  exactly the same asymptotic dependence as the SW radial function with the choice  $\sigma_F = 4\gamma_{SW}/\delta = 8.3804$ .

The inverted radial function  $g(r)$  for the  $\beta$ -tin lattice is shown Fig. 1(c). Notice that  $r_{min}$ , the minimum radius for validity of the inversion, is around 2.2  $\text{\AA}$ , where second neighbor contributions in the diamond lattice become important. The inverted curve starts out very close to SW near the cutoff radius; it peaks around the nearest neighbor distances (both shells 1 and 2 contribute to the coordination,  $n_1 + n_2 = 2 + 4 = 6$ ) and becomes smaller at decreasing radii. This behavior is in contrast to most empirical potentials which have monotonic radial functions like SW. We have observed similar behavior by inverting energies for other lattices as well as different angular dependences. Thus, we have theoretical evidence that the many-body radial function should be peaked at roughly the first neighbor distance, *i.e.* the strength of bond-bending forces is largest at the equilibrium distance and decreases when bonds are either stretched or compressed.

## DISCUSSION AND CONCLUSION

Although the inversion procedure is exact, it does not necessarily produce a realistic potential. The reason is that it requires the cluster expansion to be valid over the entire range of atomic volumes from solid to gas, producing a potential of artificially long range, which can be understood as follows: Because the solution begins at the cutoff and proceeds to smaller distances, the tail of the inverted potential comes from the energy of a greatly

expanded crystal whose first neighbors are near the cutoff. This tail is then used to describe interactions with higher shells in determining the potential at the nearest neighbor distance in the equilibrium solid. The problem is that long-range interactions in a solid are screened compared to isolated atoms at the same separation.

For semiconductors like Si, which require higher orders of cluster expansion, the problem is even more serious. The angular dependence of cluster potentials is intended to describe bond-bending forces, primarily for  $sp^3$  hybrid orbitals, in condensed phases. However, when the crystal is expanded so that the atoms are well isolated, covalent bonding between hybrids is presumably replaced by a more spherically symmetric, metallic type interaction. Thus, we would not expect the inversion procedure with a long range to produce a reasonable three-body radial function  $g(r)$ . From these considerations, the introduction of a cutoff function in the manner described above is motivated by physical requirements.

We propose that this procedure of determining the effective interatomic potential is closer to first-principles than other approaches that rely on arbitrarily chosen functional forms with many adjustable parameters. Moreover, the procedure can be generalized to handle anisotropic structures (for  $\phi(r)$  at least) as well as other classes of cluster potentials and cluster functionals. By comparing the inverted pair potentials  $\phi(r)$  for multiple crystals, information on the environmental dependence of bond strengths can be extracted. A comparison of radial functions  $g(r)$  for multiple crystals is equally interesting. The degree of similarity of the inverted radial functions for a particular choice of  $h(\theta)$  is a parameter-free quantitative measure of how well the angular dependence can describe the energetics of volume expansions in different bulk phases.

In conclusion, we have described a procedure for inverting *ab initio* cohesive energy vs. volume curves to obtain the radial functions of a cluster potential that exactly reproduces the curves with a given angular function. The procedure generalizes a recursive proof of the CGE pair potential formula. We have inverted LDA curves for diamond and  $\beta$ -tin silicon resulting in an *ab initio* cluster potential with the SW angular dependence, and have briefly discussed strengths and weaknesses of the procedure.

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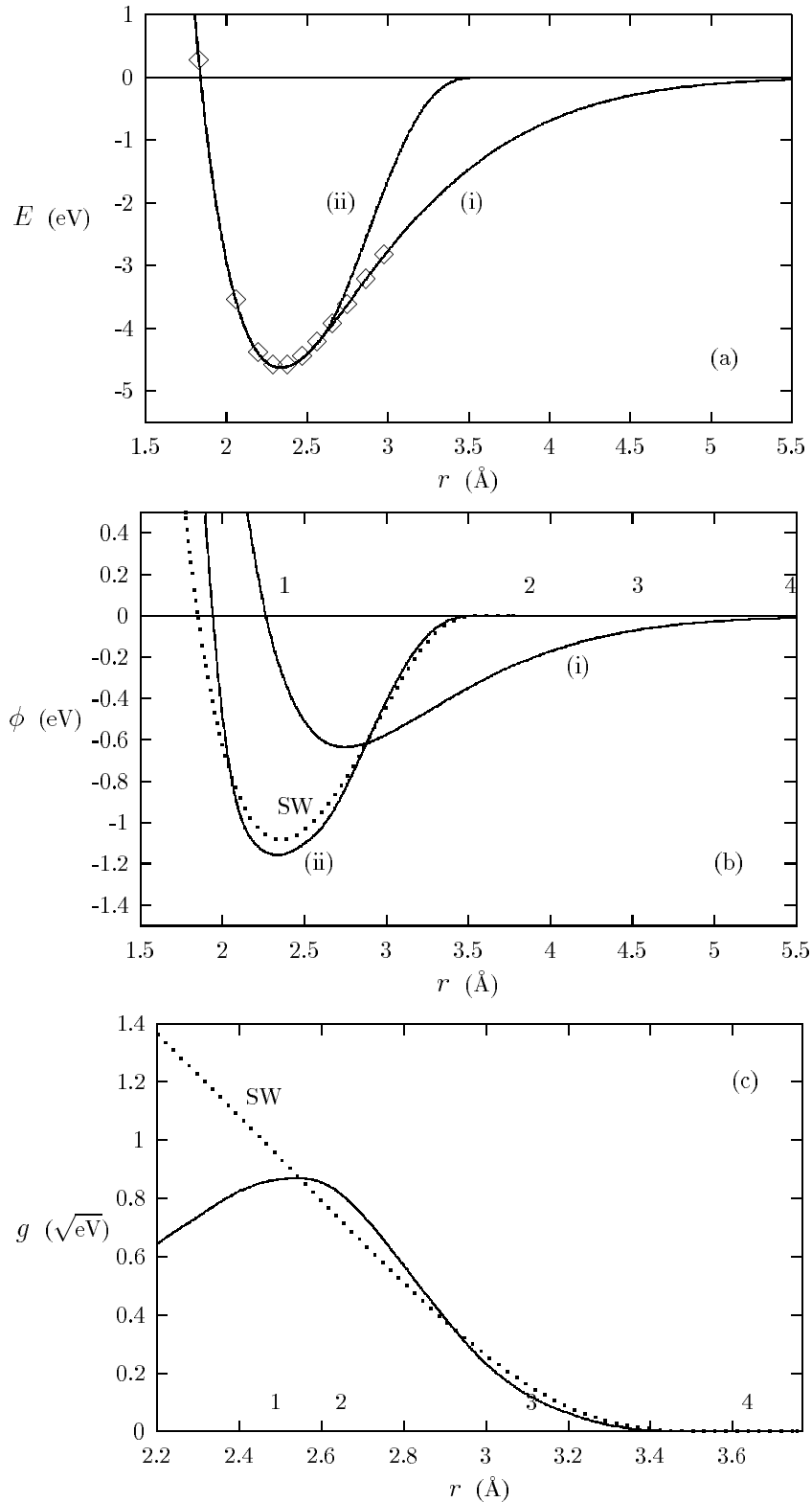


Figure 1: An *ab initio* cluster potential for silicon: (a) the diamond LDA energy data vs. first neighbor distance ( $\diamond$ ), the interpolant without (i) and with (ii) the SW cutoff; (b) the inverted pair potentials that exactly reproduce (i) and (ii), the SW pair potential, numbers  $p = 1 - 4$  marking equilibrium diamond shell radii; (c) the inverted radial function the reproduces the  $\beta$ -tin LDA data with the SW cutoff (not shown) assuming the SW angular factor, the SW radial function; numbers marking equilibrium  $\beta$ -tin shell radii.