

Tight-Binding Bond Order Potential and Forces for Atomistic Simulations

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The formalism of a new bond order potential is described in detail, including very recent developments—most notably the implementation of a numerically stable recursive algorithm for obtaining the coefficients of the many-atom expansion. This tight-binding Green's function method is efficient, the computer time scaling linearly with number of atoms. Technical notes on the proof of the central results and on handling the integration of Green's functions are attached.

Introduction

Atomistic simulations of the structure of large systems at all times need potentials that are simple and accurate over a wide range of geometry and coordination. Tersoff has proposed an analytical interatomic potential for Si (Ref 1). The form of this empirical potential was motivated by the role of the bond order and its dependence on local environment. Because the directionality of bonding in covalently bonded systems comes from their electronic structure, more information about the electronic structure should be taken into account if the potentials

are to be accurate enough to handle not only Si, but other semiconducting elements, transition metals, and their compounds. The simplest reasonable way to describe the electronic structure of molecules and nonsimple metals is to employ the tight-binding (TB) theory (Ref 2).

There are a couple of key concepts about the scaling of computation time, which categorize the methods of obtaining the energy. The first concept is the scaling of computation time with system size. More precisely, how the number of arithmetic operations grows with system size N , the number of inequivalent atoms in the supercell, in the limit of large N . Clearly, with classical or empirical interatomic potentials, having an appropriate cut-off radius imposed, the computation time for energy scales like $O(N)$, that is, linearly with system size N . Whereas, typical methods for the eigenvalue problem of a matrix leads to an $O(N^3)$ workload. Recently, new quantum-mechanical $O(N)$ methods have been sought (Ref 3-6). The second concept, which is related to the use of a parallel computer or the cluster of computers, is the scaling of computation time with the number of parallel processors P . Ideally, one would have $o(P^{-1})$ scaling. The method described in this paper belongs to the category of $O(N)$ and $o(P^{-1})$ (see Fig. 1).

From the viewpoint of these two concepts, the TB recursion method (Ref 7-9) has superiority over the conventional k -space TB method as it is an $O(N)$ method. The TB recursion method is designed to obtain most efficiently the local electronic structure, which represents the diagonal Green's functions $G^{I,I}$ in continued fraction form, and also the intersite Green's functions $G^{I,J}$ directly from the difference, $\frac{1}{2}(G^{I+J,I+J} - G^{I-J,I-J})$, between the continued fractions associated with bonding and antibonding orbitals. The problem of the local electronic structure about a given orbital is mapped onto the semi-infinite recursion chain model with diagonal (a_n) and subdiagonal (b_n) coefficients. In practice, these are often approximated from some level by repeating constants (a_∞ and b_∞) for an infinite number of levels, so that the continued fraction is terminated. However, it was a drawback to the TB recursion method that the convergence of the

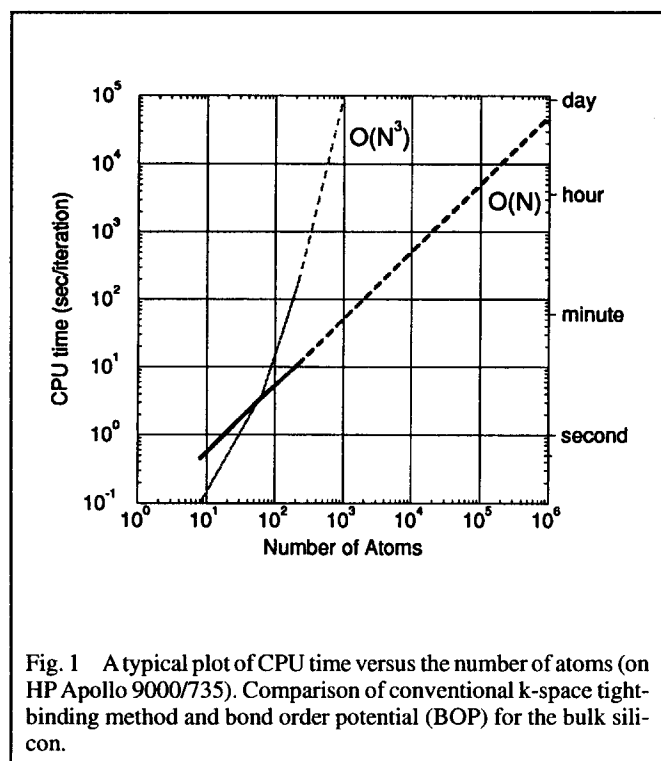


Fig. 1 A typical plot of CPU time versus the number of atoms (on HP Apollo 9000/735). Comparison of conventional k -space tight-binding method and bond order potential (BOP) for the bulk silicon.

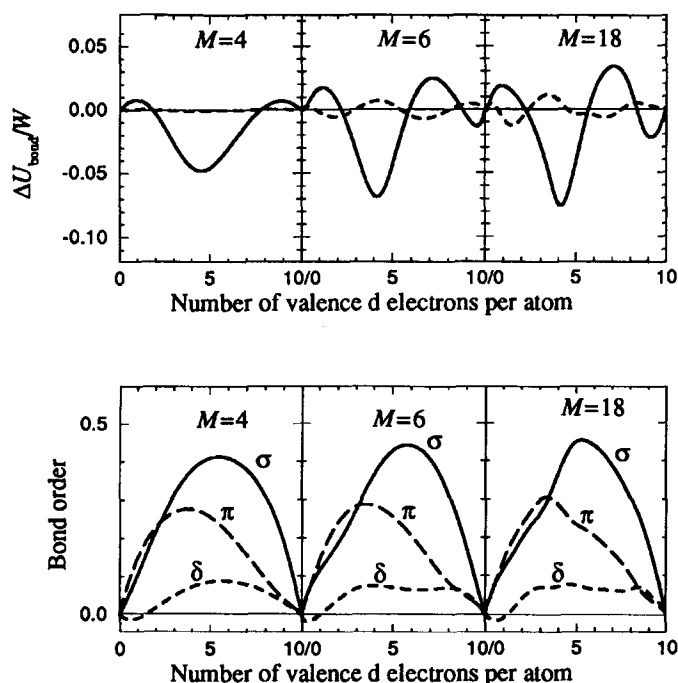


Fig. 2 Upper panels: Convergence of TB bond energy differences for bcc, cph, and fcc structures (solid and dashed lines for bcc-fcc and cph-fcc, respectively) with the fourth, sixth, and eighteenth moment approximations. W is the nominal band width of the canonical d band model. Lower panels: Convergence of σ , π , and δ bond orders between the nearest neighbors in d -bonded fcc lattice.

bond order and the Hellmann-Feynman force and even the energy calculated from intersite Green's function was very poor (Ref 10).

In 1989, Pettifor derived a new, simple quantum-mechanical interatomic potential for covalently bonded materials (Ref 11). The central result of this was a novel method for expanding the bond order as a many-atom expansion, in which one can see the contributions to the bond order from n -membered rings of atoms. Because this many-atom expansion in the original form was only justified within first-order perturbation theory on the continued fraction, it was further developed (Ref 12) and then proved to be exact (Ref 13). An important question was how can one truncate a many-atom expansion that is exact but continues infinitely. The importance of a sum rule for intersite Green's function was then pointed out, and its power was demonstrated for simple s and sp -valent equivalent-site systems (Ref 14, 15). Recently, a generalized theory of the many-atom expansion was presented (Ref 16) with a simple way to truncate the expansion that guarantees the sum rule. Convergence of the energy and the bond order using the new many-atom expansion is displayed in Fig. 2.

Bond order potential (BOP) is the generic name for the TB many-atom potentials based on the new method of many-atom expansion for the bond order, which has been developed since 1989. The aim of this paper is to present the details of the theory of BOP, including very recent developments such as an implementation of a numerically stable recursive algorithm for obtaining the coefficients of the many-atom expansion. Some

details of the proof, handling polynomials, and semi-analytic integrals of the Green's functions are given in the Appendices to this article.

Background

Tight-Binding Recursion Method

The well-known Lanczos algorithm is an efficient and numerically stable method for obtaining the exact or approximate eigenvalues of a sparse matrix such as the relatively short-range (TB) Hamiltonian. Setting up a starting state vector $|u_0\rangle$, which can be any linear combination of atomic orbitals (usually a single orbital), the algorithm proceeds as follows:

$$H|u_0\rangle = a_0|u_0\rangle + b_1|u_1\rangle \quad (\text{Eq 1})$$

$$H|u_1\rangle = b_1|u_0\rangle + a_1|u_1\rangle + b_2|u_2\rangle \quad (\text{Eq 2})$$

⋮

$$H|u_n\rangle = b_n|u_{n-1}\rangle + a_n|u_n\rangle + b_{n+1}|u_{n+1}\rangle \quad (\text{Eq 3})$$

Each step generates a new normalized vector that is orthogonal to all the preceding vectors ($\langle u_m | u_n \rangle = \delta_{n,m}$). Coefficients a and b are called recursion coefficients, representing the diago-

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nal and subdiagonal elements of tridiagonalized Hamiltonian as:

$$a_n = \langle u_n | H | u_n \rangle \quad (\text{Eq 4})$$

$$b_n = \langle u_{n-1} | H | u_n \rangle \quad (\text{Eq 5})$$

Using these recursion coefficients, a continued fraction expression is obtained for the diagonal Green's function (the diagonal elements of the Greenian $G(E) = (E - H)^{-1}$) as:

$$G_{00}(E) \equiv \langle u_0 | G(E) | u_0 \rangle = \frac{1}{E - a_0 - \frac{(b_1)^2}{E - a_1 - \frac{(b_2)^2}{E - a_2 - \dots}}} \quad (\text{Eq 6})$$

The density of states per spin associated with the starting state vector is simply given by:

$$n_0(E) = -\frac{1}{\pi} \text{Im} G_{00}(E + i0) \quad (\text{Eq 7})$$

The number of electrons fractionally occupying the state is:

$$N_0(E) = -\frac{1}{\pi} \text{Im} \int_{-\infty}^{E_F} G_{00}(E + i0) dE \quad (\text{Eq 8})$$

where E_F denotes the Fermi level of the system.

Except for very simple and finite systems, one may have to terminate the recursion after some feasible number of steps to guess the tail of the continued fraction. Sometimes a simple functional form for the tail is a good guess. The so-called square root terminator (SRT) is often used as an approximate tail, where all the diagonal and subdiagonal recursion coefficients are approximated by some reasonable constants a_∞ and b_∞ , respectively. The continued fraction is then terminated with the last level:

$$E - a_N - \frac{1}{2} \left[(E - a_\infty) - \sqrt{(E - a_\infty - 2b_\infty)(E - a_\infty + 2b_\infty)} \right] \quad (\text{Eq 9})$$

How many recursion levels should be reached? The higher the number of levels we include, the more accurate the energy we can expect, of course. But the more levels that are included, the more computer time and memory consumed. The following consideration may be helpful. The shape of the density of states can be characterized by its moments defined by:

$$\mu_r \equiv \int_{-\infty}^{\infty} E^r n_0(E) dE = \langle u_0 | \overbrace{HH \dots H}^r | u_0 \rangle \quad (\text{Eq 10})$$

The last expression means that the r th moment of the density of states has a direct connection to the collection of all the paths of length r starting from the initial orbital and coming back to the same orbital. Regardless of choice of terminator,

the continued fraction preserves exact moments to $\mu_{2n+1}(\mu_{2n})$ if the recursion coefficients are exact to $a_n(b_n)$. Ducastelle's moment theorem (Ref 17 and the original reference therein) is a very powerful tool for understanding the meaning of moments when comparing cohesive energies of different structures. This theorem states that if two densities of states have their first n moments identical then the energy difference curve as a function of band filling must have at least $n - 1$ nodes. Therefore, one has to include the exact moments that are enough to predict the stable structure correctly. For example, for a given transition metal element the TB theory with the canonical d -band parameters predicts that the energy difference between bcc and fcc structures has two prominent nodes and that between cph and fcc structures basically has four nodes. In fact, the fourth moment of the density of states makes a clear distinction in the case of bcc versus fcc, and the sixth moment in the case of cph versus fcc.

Energy, Bond Order, and Force

There are two different expressions for the same quantity, the covalent bond energy. Using the diagonal Green's function:

$$G^{II}(E) = \langle \phi^I | G(E) | \phi^I \rangle \quad (\text{Eq 11})$$

which is nothing but G_{00} associated with starting atomic orbital ϕ^I on atom i (I is used as the site and the orbital index), the covalent bond energy of the system will be given by the sum of energies of atoms, namely:

$$U_{\text{bond}} = \sum_i -\frac{2}{\pi} \text{Im} \int_{-\infty}^{E_F} (E - E^I) G^{II}(E + i0) dE \quad (\text{Eq 12})$$

where $E^I = H^{II}$ is the energy of an atomic orbital. The factor of 2 represents the spin degeneracy. An alternative expression for the bond energy can be given by the sum of energies of individual bonds, namely:

$$U_{\text{bond}} = \frac{1}{2} \sum_{I \neq J} 2H^{IJ} \Theta^{IJ} \quad (\text{Eq 13})$$

with the bond order given by:

$$\Theta^{IJ} = -\frac{1}{\pi} \text{Im} \int_{-\infty}^{E_F} 2G_{IJ}(E + i0) dE \quad (\text{Eq 14})$$

using the intersite Green's functions:

$$G^{IJ}(E) = \langle \phi^I | G(E) | \phi^J \rangle \quad (\text{Eq 15})$$

Equivalence of the two expressions is guaranteed by the operator identity $(E - H)G(E) = 1$, which is written in orbital representation as:

$$(E - H^{II})G^{II}(E) = 1 + \sum_{J(I \neq J)} H^{IJ} G^{IJ}(E) \quad (\text{Eq 16})$$

This relation is very important when one is to make some approximation to the Green's functions. As was mentioned above, the diagonal Green's function is often approximated by a terminated continued fraction. If one attempts to obtain the intersite Green's function from the difference between the terminated continued fractions associated with bonding orbital ($2^{-1/2}(\phi^I + \phi^J)$) and antibonding orbital ($2^{-1/2}(\phi^I - \phi^J)$), then the right-hand side of Eq 16 will no longer be guaranteed to equal the left-hand side. This is the origin of the poor convergence in the conventional intersite recursion method. Equation 16 is referred to as the "sum rule." In the following, the new method is used to calculate intersite Green's functions that are able to fulfill the sum rule.

An advantage of use of the bond order is that the Hellmann-Feynman (HF) expression:

$$F_k = -\frac{1}{2} \sum_I \sum_J 2 \left(\frac{\partial H^{I,J}}{\partial R_k} \right) \Theta^{J,I}(E_F) \quad (\text{Eq 17})$$

for the force can be used if the bond order is accurate enough. Numeric force, that is, the force calculated by numerical differentiation of the total energy, has to be far more expensive for molecular dynamics than the HF force.

Core of BOP Formalism

Generalized Exact Many-Atom Expansion

Let us begin with the central theorem for deriving the new many-atom expansion for the intersite Green's function.

Theorem. Consider two Hilbert spaces: a space spanned by atomic orbitals ($H_{ao} = \{\Phi^I\}$) and an auxiliary space ($H_{aux} = \{e_I\}$) whose elements have a one-to-one correspondence with the orthonormal atomic orbitals. We may define a new vector:

$$|w_0^\Lambda\rangle = \sum_I |\Phi^I\rangle |e_I\rangle \quad (\text{Eq 18})$$

in the direct product space $H_o \otimes H_{ao} \otimes H_{aux}$. For any operator Q acting on H_{ao} , we obtain:

$$Q_{00}^\Lambda \equiv \{w_0^\Lambda | Q | w_0^\Lambda\} = \sum_{I,J} \langle \Phi^I | Q | \Phi^J \rangle (e_I | e_J) = \sum_{I,J} Q^{J,I} \Lambda_{J,I} \quad (\text{Eq 19})$$

with

$$\Lambda_{J,I} \equiv (e_I | e_J) \quad (\text{Eq 20})$$

We then establish:

$$Q^{J,I} = \frac{\partial Q_{00}^\Lambda}{\partial \Lambda_{J,I}} \quad (\text{Eq 21})$$

Many-Atom Expansion. Taking Eq 18 as a starting vector, we apply the Lanczos recursion algorithm in the direct product space, that is:

$$H | w_n^\Lambda \rangle = b_n^\Lambda | w_{n-1}^\Lambda \rangle + a_n^\Lambda | w_n^\Lambda \rangle + b_{n+1}^\Lambda | w_{n+1}^\Lambda \rangle \quad (\text{Eq 22})$$

with the condition that:

$$\{w_m^\Lambda | w_n^\Lambda\} = \delta_{m,n} \quad (\text{Eq 23})$$

and $|w_{-1}^\Lambda\rangle = 0$. The recursion vectors and coefficients are now dependent on the choice of Λ . Using these recursion coefficients, the diagonal Green's function defined by:

$$G_{00}^\Lambda(E) = \{w_0^\Lambda | G | w_0^\Lambda\} \quad (\text{Eq 24})$$

can be written as a continued fraction in the same form as Eq 6. By the theorem described above, the off-diagonal elements of the Greenian can be derived as a form of many-atom expansion as follows:

$$\begin{aligned} G^{J,I} &= \frac{\partial G_{00}^\Lambda}{\partial \Lambda_{J,I}} = \sum_{n=0}^{\infty} \frac{\partial G_{00}^\Lambda}{\partial a_n^\Lambda} \frac{\partial a_n^\Lambda}{\partial \Lambda_{J,I}} + \sum_{n=1}^{\infty} \frac{\partial G_{00}^\Lambda}{\partial b_n^\Lambda} \frac{\partial b_n^\Lambda}{\partial \Lambda_{J,I}} \\ &= \sum_{n=0}^{\infty} G_{0n}^\Lambda G_{n0}^\Lambda \alpha_n^{\Lambda,J,I} + \sum_{n=1}^{\infty} G_{0(n-1)}^\Lambda G_{n0}^\Lambda 2\beta_n^{\Lambda,J,I} \quad (\text{Eq 25}) \end{aligned}$$

The bond order is now written as:

$$\Theta^{J,I} = -2 \left[\sum_{n=0}^{\infty} \chi_{0n,n0}^\Lambda \alpha_n^{\Lambda,J,I} + \sum_{n=1}^{\infty} \chi_{0n-1,n0}^\Lambda 2\beta_n^{\Lambda,J,I} \right] \quad (\text{Eq 26})$$

where the response functions are defined by:

$$\chi_{0m,n,0}^\Lambda = \frac{Im}{\pi} \int_{E_F} G_{0m}^\Lambda(E + i0) G_{n0}^\Lambda(E + i0) dE \quad (\text{Eq 27})$$

These response functions, together with the number of electrons, can be calculated by means of semianalytic integration described in Appendix B. Coefficients α and β are defined by:

$$\alpha_n^{\Lambda,J,I} = b_{n+1}^\Lambda O_{n+1,n}^{\Lambda,J,I} - b_n^\Lambda O_{n,n-1}^{\Lambda,J,I} \quad (\text{Eq 28})$$

$$\beta_n^{\Lambda,J,I} = b_n^\Lambda \left(O_{n,n}^{\Lambda,J,I} - O_{n-1,n-1}^{\Lambda,J,I} \right) \quad (\text{Eq 29})$$

with

$$O_{m,n}^{\Lambda,J,I} = \langle \Phi^I | P_m^\Lambda(H) P_n^\Lambda(H) | \Phi^I \rangle \quad (\text{Eq 30})$$

$P_n(x)$ is orthogonal polynomials defined by:

$$x P_n^\Lambda(x) = b_n^\Lambda P_{n-1}^\Lambda(x) + a_n^\Lambda P_n^\Lambda(x) + b_{n+1}^\Lambda P_{n+1}^\Lambda(x) \quad (\text{Eq 31})$$

with $P_{-1}^\Lambda(x) = 0$ and $P_0^\Lambda(x) = 1$.

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The elements of the O -matrix can be calculated from boundary values of $O_{n,0}^{\Lambda,J,I}$ making use of a recursive relation:

$$b_m^{\Lambda} O_{m,n}^{\Lambda,J,I} + a_{m-1}^{\Lambda} O_{m-1,n}^{\Lambda,J,I} + b_{m-1}^{\Lambda} O_{m-2,n}^{\Lambda,J,I} = b_{n+1}^{\Lambda} O_{m-1,n+1}^{\Lambda,J,I} + a_n^{\Lambda} O_{m-1,n}^{\Lambda,J,I} + b_n^{\Lambda} O_{m-1,n-1}^{\Lambda,J,I} \quad (\text{Eq 32})$$

It should be noted that the O -matrix, α s and β s can be calculated simultaneously with the recursion vectors. See Appendix A for details.

Terminator, Truncator, and Sum Rule. Now we specify the particular choice of Λ . Suppose that we are interested in the intersite Green's functions between an orbital ϕ^I on the central atom i and orbitals ϕ^J on its neighbors. One choice of Λ is to let $\Lambda_{i,i} = 1$ with the other elements set to zero. This means that the recursion of Eq 22 is nothing but the conventional recursion method (RM) for the central orbital. After recursion to some level we obtain the recursion coefficients that are the same as those given by the conventional RM. We may stop recursion after obtaining the exact coefficients of b_N^{Λ} and a_N^{Λ} , and we then terminate the continued fraction with the square-root terminator. We also obtain well-defined α s and β s from Eq 28 and 29 to $\alpha_{N-1}^{\Lambda,J,I}$ and $\beta_N^{\Lambda,J,I}$. However, since $O_{n,n-1}^{\Lambda,J,I}$ and $O_{n,n}^{\Lambda,J,I}$ for $n > N + 1$ are unknown, α s and β s of higher indices remain unevaluated. In order to guarantee the sum rule by defining appropriate values for unknown coefficients, we notice that the O -matrix (see Eq A11 in Appendix A) satisfies:

$$\sum_{J(I \neq I)} H^{I,J} O_{n,n}^{\Lambda,J,I} = a_n^{\Lambda} - a_0^{\Lambda} \quad (\text{Eq 33})$$

$$\sum_{J(I \neq I)} H^{I,J} O_{n-1,n}^{\Lambda,J,I} = b_n^{\Lambda} \quad (\text{Eq 34})$$

We easily find that if we define approximate $O_{n,n}^{\Lambda,J,I}$ and $O_{n-1,n}^{\Lambda,J,I}$ so as to yield $a_{\infty}^{\Lambda} - a_0^{\Lambda}$ and b_{∞}^{Λ} , respectively, on the right-hand side of the above equations, then the sum rule is guaranteed. The simplest approximation is:

$$O_{n,n}^{\Lambda,J,I} = (a_{\infty}^{\Lambda} - a_0^{\Lambda}) H^{I,I} / (b_1^{\Lambda})^2 \quad (\text{Eq 35})$$

$$O_{n-1,n}^{\Lambda,J,I} = b_{\infty}^{\Lambda} H^{I,I} / (b_1^{\Lambda})^2 \quad (\text{Eq 36})$$

for $n \geq N + 1$. This has the effect that the many-atom expansion will automatically be truncated with the last pair of coefficients:

$$\alpha_N^{\Lambda,J,I} = (b_{\infty}^{\Lambda})^2 H^{I,I} / (b_1^{\Lambda})^2 - b_N^{\Lambda} O_{N,N-1}^{\Lambda,J,I} \quad (\text{Eq 37})$$

$$\beta_{N+1}^{\Lambda,J,I} = b_{\infty}^{\Lambda} \left[(a_{\infty}^{\Lambda} - a_0^{\Lambda}) H^{I,I} / (b_1^{\Lambda})^2 - O_{N,N}^{\Lambda,J,I} \right] \quad (\text{Eq 38})$$

These are referred to as "truncators." Notice that α s and β s of higher indices vanish.

Another choice of Λ is to let $\Lambda_{i,i} = 1/d_i$ for $(2l_i + 1)$ -fold degenerate orbitals (l_i stands for angular quantum number of atomic orbitals) of interest and naught for the other elements. This yields the rotationally invariant recursion coefficients that correspond to the moments averaged over $(2l_i + 1)$ -fold degenerate orbitals. This choice of Λ is discussed in Ref 16.

Conclusion

The authors have formulated the BOP in a most general way. Bond order potential is a TB Green's function method, for which the computation time scales like $O(N)$ and which is suitable for highly parallel computation. It is defined in terms of a numerically stable recursion algorithm and is only limited by the TB approximation. At present, however, the HF force and the numeric force yield a small but finite discrepancy at zero electronic temperature. It has very recently been shown that introduction of finite electronic temperature removes this unfavorable discrepancy (Ref 18). So far, the BOP has been tested on various systems including liquid and amorphous C, Si surfaces, and vacancies in TiC.

Acknowledgment

The authors would like to thank Peter Gumbsch, Alex Bratkovsky, Tony Paxton, and Adrian Sutton for stimulating discussions. Throughout this work, computational facilities of the Materials Modeling Laboratory (Oxford University) were used. MA wishes to thank SERC (UK) and NEDO (Japan) for financial support.

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Appendix A

α s and β s and O -Matrix

We find from Eq 22 and 31 that the recursion vectors are formally written using P -polynomials of the Hamiltonian as:

$$|w_n\rangle = P_n^\Lambda(H)|w_0\rangle = \sum_I P_n^\Lambda(H)|\phi^I\rangle|e_I\rangle \quad (\text{Eq A1})$$

Then we write the orthonormality condition:

$$\delta_{m,n} = \{w_m|w_n\} = \{w_0|P_m^\Lambda P_n^\Lambda|w_0\} \quad (\text{Eq A2})$$

and the recursion coefficients:

$$a_n^\Lambda = \{w_n|H|w_n\} = \sum_{I,J} \langle \phi^I|P_n^\Lambda H P_n^\Lambda|\phi^J\rangle \Lambda_{J,I} \quad (\text{Eq A3})$$

$$b_n^\Lambda = \{w_{n-1}|H|w_n\} = \sum_{I,J} \langle \phi^I|P_{n-1}^\Lambda H P_n^\Lambda|\phi^J\rangle \Lambda_{J,I} \quad (\text{Eq A4})$$

The coefficients α and β in the expansions Eq 25 and 26 are calculated as:

$$\alpha_n^{\Lambda,J,I} \equiv \frac{\partial a_n}{\partial \Lambda_{J,I}} = \langle \phi^I|P_n^\Lambda H P_n^\Lambda|\phi^J\rangle + 2\{w_0|\frac{\partial P_n^\Lambda}{\partial \Lambda_{J,I}} H P_n^\Lambda|w_0\} \quad (\text{Eq A5})$$

$$\begin{aligned} \beta_n^{\Lambda,J,I} \equiv \frac{\partial b_n}{\partial \Lambda_{J,I}} &= \langle \phi^I|P_{n-1}^\Lambda H P_n^\Lambda|\phi^J\rangle + \{w_0|\frac{\partial P_{n-1}^\Lambda}{\partial \Lambda_{J,I}} H P_n^\Lambda|w_0\} \\ &+ \{w_0|P_{n-1}^\Lambda H \frac{\partial P_n^\Lambda}{\partial \Lambda_{J,I}}|w_0\} \end{aligned} \quad (\text{Eq A6})$$

From differentiation of the orthonormality condition, Eq A2, we obtain:

$$0 = O_{m,n}^{\Lambda,J,I} + \{w_0|\frac{\partial P_m^\Lambda}{\partial \Lambda_{J,I}} P_n^\Lambda|w_0\} + \{w_0|P_m^\Lambda \frac{\partial P_n^\Lambda}{\partial \Lambda_{J,I}}|w_0\} \quad (\text{Eq A7})$$

Because $\partial P_m^\Lambda / \partial \Lambda_{J,I}$ is a polynomial of order less than or equal to m it must be given by some linear combination of P_k^Λ with $k \leq m$. Hence, the orthonormality condition, Eq A2, tells us that:

$$\{w_0|\frac{\partial P_m^\Lambda}{\partial \Lambda_{J,I}} P_n^\Lambda|w_0\} = 0 \quad (\text{if } m < n) \quad (\text{Eq A8})$$

Substituting Eq 31 into Eq A5 and A6 to eliminate H and using Eq A7 with Eq A8, we establish useful expressions for α s and β s, namely:

$$\alpha_n^{\Lambda,J,I} = b_{n+1}^\Lambda O_{n+1,n}^{\Lambda,J,I} - b_n^\Lambda O_{n,n-1}^{\Lambda,J,I} \quad (\text{Eq A9})$$

$$\beta_n^{\Lambda,J,I} = b_n^\Lambda (O_{n,n}^{\Lambda,J,I} - O_{n-1,n-1}^{\Lambda,J,I}) \quad (\text{Eq A10})$$

The next sum rule for the O -matrix is helpful when we wish to guarantee the sum rule of Eq 16:

$$\begin{aligned} \sum_{I,J,K} H^{K,J} O_{m,n}^{\Lambda,J,I} \Lambda_{K,I} &= \sum_{I,J} \langle \phi^I|H P_m^\Lambda P_n^\Lambda|\phi^J\rangle \langle e_J|e_I\rangle \\ &= \{w_0|H P_m^\Lambda P_n^\Lambda|w_0\} \\ &= \{w_m|H|w_n\} \\ &= \begin{cases} b_n^\Lambda (m = n-1) \\ a_n^\Lambda (m = n) \\ b_{n+1}^\Lambda (m = n+1) \\ 0 \text{ (otherwise)} \end{cases} \end{aligned} \quad (\text{Eq A11})$$

From the identity

$$\langle \phi^I|P_m^\Lambda (H P_n^\Lambda)|\phi^J\rangle = \langle \phi^I|(P_m^\Lambda H) P_n^\Lambda|\phi^J\rangle \quad (\text{Eq A12})$$

and Eq 31, we easily get the following useful relation for the adjacent elements of the O -matrix:

$$\begin{aligned} b_m^\Lambda O_{m,n}^{\Lambda,J,I} + a_{m-1}^\Lambda O_{m-1,n}^{\Lambda,J,I} + b_{m-1}^\Lambda O_{m-2,n}^{\Lambda,J,I} \\ = b_{n+1}^\Lambda O_{m-1,n+1}^{\Lambda,J,I} + a_n^\Lambda O_{m-1,n}^{\Lambda,J,I} + b_n^\Lambda O_{m-1,n-1}^{\Lambda,J,I} \end{aligned} \quad (\text{Eq A13})$$

Using this, it is straightforward to obtain elements of the O -matrix in the triangular region shown in Fig. A1 from the boundary values:

$$O_{n,0}^{\Lambda,J,I} = \langle e_J|\phi^I|w_n\rangle \quad (n = 1 \cdots 2N) \quad (\text{Eq A14})$$

These boundary values can be obtained from a new recursion vector $|w_n\rangle$, by taking a projection of $|\phi^J\rangle|e_I\rangle$, until $n = N$. In order to calculate those values for $n = N+1$ to $2N$, we can con-

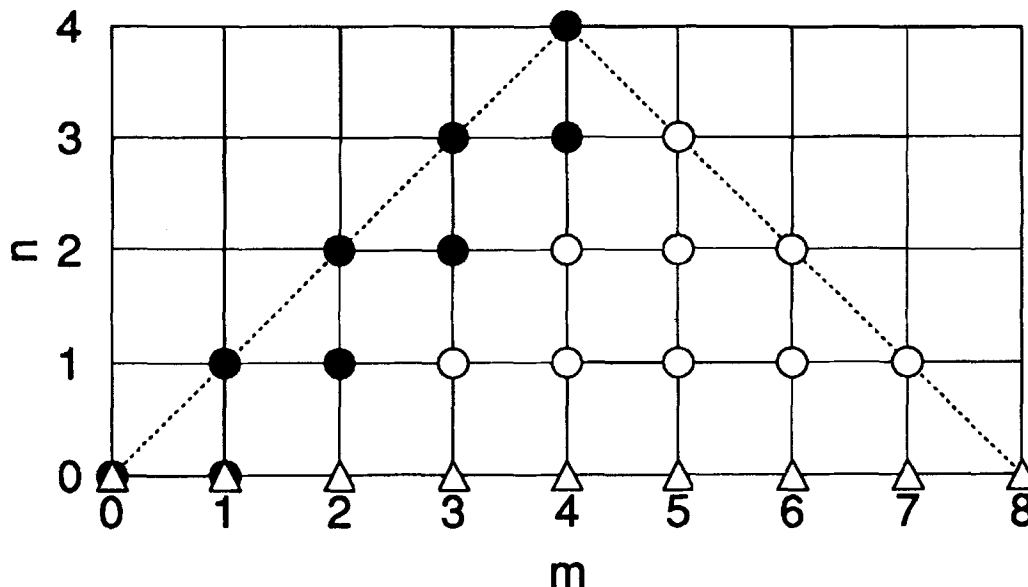


Fig. A1 Diagram for obtaining (n,n) , $(n+1,n)$ (solid circles) elements and other intermediate elements (open circles) of O -matrix recursively from the boundary $(n,0)$ elements (triangles) for the case of $N=4$.

tinue the recursion algorithm Eq 22 using fictitious recursion coefficients. For example, one may use a_∞ and b_∞ to obtain:

$$\tilde{w}_{N+1} = [H|w_N\rangle - a_N^\Lambda|w_N\rangle - b_N^\Lambda|w_N\rangle]/b_\infty \quad (\text{Eq A15})$$

where tilde is attached to indicate that the vector is given using fictitious recursion coefficients. It should be remarked that the choice of fictitious coefficients does not affect the O -matrix. It is also to be noted that there is no need to extend the size of the atomic cluster which the recursion is being performed on, because only the paths starting from atom i reaching the neighboring atom j within $2n$ -hop are to enter $O_{n,0}^{\Lambda,j,i}$.

Appendix B

Semi-Analytic Integral of Green's Function

It may in general be much faster and more accurate to evaluate analytic expressions of an integral than to do numerical quadrature. A method of analytic integration of continued fraction was developed for the case of square root termination by K. Masuda (Ref B1) and by G. Allan et al. (Ref B2) in a generalized form. The following describes a new method of analytic calculation for the number of electrons and response functions using square-root terminated continued fractions for Green's functions.

Green's Function Along the Recursion Chain. The diagonal and the off-diagonal elements of Green's functions are defined by:

$$G_{0n}(E) = \langle u_0 | (E - \hat{H})^{-1} | u_n \rangle \quad (\text{Eq B16})$$

where $|u_n\rangle$ form a set of orthonormal recursion basis, which is determined by the Lanczos-recursion algorithm (Ref 7):

$$b_{n+1}|u_{n+1}\rangle = \hat{H}|u_n\rangle - a_n|u_n\rangle - b_n|u_{n-1}\rangle \quad (\text{Eq B17})$$

with a given initial vector $|u_0\rangle$ and the condition that $|u_{-1}\rangle$ vanishes. a_n and b_n are the recursion coefficients, which lead to the continued fraction expression for the diagonal Green's function (Ref 8, 9):

$$G_{00}(Z) = \frac{1}{Z - a_0 - \frac{(b_1)^2}{Z - a_1 - \frac{(b_2)^2}{Z - a_2 - \dots}}} \quad (\text{Eq B18})$$

This can be also written in the other form (Ref 9):

$$G_{00}(Z) = \frac{Q_L(Z) - Q_{L-1}(Z)b_L G_L(Z)}{b_1[P_L(Z) - P_{L-1}(Z)b_L G_L(Z)]} \quad (\text{Eq B19})$$

where $P_n(Z)$ and $Q_n(Z)$ are polynomials of Z defined by:

$$b_{n+1}P_{n+1} = (E - a_n)P_n - b_nP_{n-1} \quad (\text{Eq B20})$$

with $P_{-1} = 0$ and $P_0 = 1$, and:

$$b_{n+1}Q_{n+1} = (E - a_n)Q_n - b_nQ_{n-1} \quad (\text{Eq B21})$$

with $Q_0 = 0$ and $Q_1 = 1$. Explicit expressions for P and Q are given by determinants:

$$P_n(Z) = (b_1 \dots b_n)^{-1} \begin{vmatrix} Z - a_0 & -b_1 & & 0 \\ -b_1 & Z - a_1 & \ddots & \\ 0 & \ddots & -b_{n-1} & Z - a_{n-1} \end{vmatrix} \quad (\text{Eq B22})$$

and

$$Q_n(Z) = (b_2 \dots b_n)^{-1} \begin{vmatrix} Z - a_1 & -b_2 & & 0 \\ -b_2 & Z - a_2 & \ddots & \\ 0 & \ddots & -b_{n-1} & Z - a_{n-1} \end{vmatrix} \quad (\text{Eq B23})$$

$b_L G_L(Z)$ is the “tail” of the continued fraction defined by:

$$b_L G_L(Z) = \frac{b_L}{Z - a_L - \frac{(b_{L+1})^2}{Z - a_{L+1} - \dots}} \quad (\text{Eq B24})$$

Following the Lanczos-recursion algorithm, Eq B17, we find the following recurrence relation:

$$b_{n+1} G_{0(n+1)}(Z) = (Z - a_n) G_{0n}(Z) - b_n G_{0(n-1)}(Z) - \delta_{0,n} \quad (\text{Eq B25})$$

It follows from Eq B20, B21, and B25 that:

$$G_{0n}(Z) = P_n(Z) G_{00}(Z) - Q_n(Z) / b_1 \quad (\text{Eq B26})$$

Using Eq B19 we find:

$$G_{0n}(Z) = \frac{Q_L^n(Z) - Q_{L-1}^n(Z) b_L G_L(Z)}{b_1 [P_L(Z) - P_{L-1}(Z) b_L G_L(Z)]} \quad (\text{Eq B27})$$

where another polynomial defined by:

$$Q_m^n = P_n Q_m - P_m Q_n \quad (\text{Eq B28})$$

is used. Q_m^n has the following properties, namely:

$$Q_m^n = -Q_m^n \quad (\text{Eq B29})$$

and

$$b_{n+1} Q_m^{n+1} = (Z - a_n) Q_m^n - b_n Q_m^{n-1} \quad (\text{Eq B30})$$

It can be easily proved that:

$$Q_m^n = 0 \quad (\text{Eq B31})$$

$$Q_{n+1}^n = b_1 / b_{n+1} \quad (\text{Eq B32})$$

For the case $m > n$, we can write:

$$Q_m^n(Z) = \frac{b_1}{b_{n+1} \dots b_m} \begin{vmatrix} Z - a_{n+1} & -b_{n+2} & & 0 \\ -b_{n+2} & Z - a_{n+2} & \ddots & \\ 0 & \ddots & -b_{m-1} & Z - a_{m-1} \end{vmatrix} \quad (\text{Eq B33})$$

Finally, we note $Q_m^0 = Q_m$.

The Square Root Terminator. If we make an approximation that the “tail” of continued fraction is that of constant semi-infinite linear chain, namely:

$$a_L = a_{L+1} = \dots = a \quad (\text{Eq B34})$$

then the tail becomes:

$$b_L G_L(Z) = T(Z) = b[Z - a - bT(Z)]^{-1} \quad (\text{Eq B35})$$

T is the so-called square root terminator (SRT), which is written as:

$$T(Z) = t(z) = z - \sqrt{z-1} \sqrt{z+1} \quad (\text{Eq B36})$$

with

$$z \equiv \frac{Z - a}{2b} \quad (\text{Eq B37})$$

Now, with the SRT we write:

$$G_{0n} = \frac{Q_L^n - Q_{L-1}^n T}{b_1 [P_L - P_{L-1} T]} \quad (\text{Eq B38})$$

If $n \geq L - 1$ the expression further simplifies to:

$$G_{0n} = \frac{T^{n-(L-1)}}{b[P_L - P_{L-1} T]} \quad (\text{Eq B39})$$

This is obtained using:

$$Q_L^n - Q_{L-1}^n T = T^{n-(L-1)} b_1 / b \quad (\text{Eq B40})$$

which can be proved as follows. For $n = L - 1$ Eq B39 is trivial from Eq B31 and B32. Also $n = L$ is another trivial case. For $n > L$ we find from Eq B30, B34, and B36:

$$Q_{L-1}^n = 2z Q_{L-1}^{n-1} - Q_{L-1}^{n-2} = (T + T^{-1}) Q_{L-1}^{n-1} - Q_{L-1}^{n-2}.$$

We notice here that $Q_{L-1}^{n-1} = Q_L^n$ and $Q_{L-1}^{n-2} = Q_L^{n-1}$ as they only use the constant tail of the chain. Therefore:

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$$\begin{aligned} Q_L^n - Q_{L-1}^n T &= (Q_L^n - Q_{L-1}^{n-1} + (Q_{L-1}^{n-2} - Q_{L-1}^{n-1})T)T \\ &= (Q_L^{n-1} - Q_{L-1}^{n-1})T \\ &= T^{n-(L-1)}b_1/b \end{aligned}$$

t Integral. Let us define lower-case dimensionless functions by upper-case functions as follows:

$$g_{0n}(z) = b_1 G_{0n}(Z) = b_1 G_{0n}(2bz + a) \quad (\text{Eq B41})$$

$$p_n(z) = P_n(Z) = P_n(2bz + a) \quad (\text{Eq B42})$$

$$q_m^n(z) = Q_m^n(Z) = Q_m^n(2bz + a) \quad (\text{Eq B43})$$

The Green's function as a function of z includes the complex square root of $z \pm 1$. The straightforward way to integrate the Green's function is to rationalize its denominator by multiplying by its conjugate, that is, $p_L - p_{L-1}(z + \sqrt{z-1}\sqrt{z+1})$. Even having done this, the square root function still remains in the numerator. It is useful to notice that the Green's function can be regarded as a completely rational function of t which was defined by Eq B36. The variable z is then replaced by:

$$z \equiv \frac{1}{2} \left(t + \frac{1}{t} \right) \quad (\text{Eq B44})$$

An integral of a function of z and $t(z)$ over the complex energy Z can be performed choosing t as an independent variable of integration. Before doing this, some remarks may be necessary.

First, notice that complex function $t(z)$ is defined with the Riemann plane of z , consisting of two sheets interconnected along the branch cut between -1 and $+1$. Second, the upper sheet defines physical Green's function in a sense that $2t(z) \sim 1/z$ when $|z|$ tends to infinity, whereas the lower sheet does not. Third, if z is at any points on the upper (lower) sheet, then $|t(z)| < 1$ ($|t(z)| > 1$). Therefore, the physical upper z -plane is mapped onto the inside of the unit circle in the t -plane, and the lower z -plane onto the outside of the circle. The real axis is mapped either onto the real axis or onto the unit circle in the t -plane. By the Herglotz property the Green's function does not have singularities except on the real axis. That means, there are no singularities inside the unit circle except along the real axis in the t -plane. Outside the circle and on the real axis, there can be singularities such as poles.

For the calculation of the number of electrons, we may use:

$$\int dZ G_{00}(Z) = \frac{b}{b_1} \int g_{00} \left(\frac{t^2 + 1}{2t} \right) \frac{t^2 - 1}{t^2} dt \quad (\text{Eq B45})$$

For the calculation of the bond energy:

$$\int dZ b_1 G_{01}(Z) = b \int g_{01} \left(\frac{t^2 + 1}{2t} \right) \frac{t^2 - 1}{t^2} dt \quad (\text{Eq B46})$$

Finally, for the response functions:

$$\int dZ G_{0m}(Z) G_{n0}(Z) = \frac{b}{b_1^2} \int g_{0m} \left(\frac{t^2 + 1}{2t} \right) g_{0n} \left(\frac{t^2 + 1}{2t} \right) \frac{t^2 - 1}{t^2} dt \quad (\text{Eq B47})$$

These integrands are perfectly rationalized. In order to express $g_{0n}((t^2 + 1)/2t)$ in a fraction of polynomials, let us introduce polynomials of t defined by:

$$\tilde{p}_n(t) = t^n p_n \left(\frac{t^2 + 1}{2t} \right) \quad (\text{Eq B48})$$

and

$$\tilde{q}_m^n(t) = t^{m-n-1} q_m^n \left(\frac{t^2 + 1}{2t} \right) \quad (\text{Eq B49})$$

Note that degree of $q_m^n(z)$ ($m \neq n$) is $|m - n| - 1$, therefore $\tilde{q}_m^n(t)$ is not polynomial if $n > m$; in fact it is a polynomial of degree $2(n - m - 1)$ divided by $t^{2(n-m)}$. However, this causes no problem in the following calculations and we leave this as it is. These polynomials follow the recurrence rules:

$$\frac{b_{n+1}}{b} \tilde{p}_{n+1} = (t^2 + 1 - \frac{a_n - a}{b} t) \tilde{p}_n - t^2 \frac{b_n}{b} \tilde{p}_{n-1} \quad (\text{Eq B50})$$

with $\tilde{p}_{-1} = 0$ and $\tilde{p}_0 = 1$, and

$$\frac{b_n}{b} \tilde{q}_m^{n-1} = (t^2 + 1 - \frac{a_n - a}{b} t) \tilde{q}_m^n - t^2 \frac{b_{n+1}}{b} \tilde{q}_m^{n+1} \quad (\text{Eq B51})$$

with $\tilde{q}_m^m = 0$ and $\tilde{q}_m^{m-1} = b_1/b_m$.

Green's function can now be given in a simple form:

$$g_{0n} \left(\frac{t^2 + 1}{2t} \right) = \frac{t^{n+1} R_L^n(t)}{F_L(t)} \quad (\text{Eq B52})$$

with polynomials:

$$F_L(t) = \tilde{p}_L(t) - t^2 \tilde{p}_{L-1}(t) \quad (\text{Eq B53})$$

and

$$R_L^n(t) = \tilde{q}_L^n(t) - t^2 \tilde{q}_{L-1}^n(t) \quad (\text{Eq B54})$$

Note that $R_L^n(t)$ is polynomial for any $n \geq 0$. It can be easily proved from Eq B40 that:

$$R_L^n(t) = b_1/b \text{ (if } n \geq L - 1) \quad (\text{Eq B55})$$

With initial values of $R_L^{L-1} = R_L^L = b_1/b$, we can calculate the polynomial by the same recurrence rule for \tilde{q}^s , namely:

$$\frac{b_n}{b} R_L^{n-1} = \left(t^2 + 1 - \frac{a_n - a}{b} t \right) R_L^n - t^2 \frac{b_{n+1}}{b} R_L^{n+1} \quad (\text{Eq B56})$$

Partial Fraction Decomposition of R_L^n/F_L . Given the roots of $F_L(t_r) = 0$, R_L^n/F_L can be decomposed into partial fractions as:

$$\frac{R_L^n(t)}{F_L(t)} = \sum_{r=1}^M \frac{R_L^n(t_r)}{F_L'(t_r)} \frac{1}{t-t_r} \quad (\text{Eq B57})$$

where $M(\leq 2L-1)$ is the degree of polynomial $F_L(t)$ and $F_L'(t)$ is derivative. Note that the degree of $R_L^n(t)$ ($\leq 2L-3$) is less than that of $F_L(t)$. A product of Green's functions can also be decomposed using:

$$\frac{R_L^m(t)R_L^n(t)}{F_L^2(t)} = \sum_{r=1}^M \frac{1}{F_L'(t_r)} \left\{ \frac{R_L^m(t_r)R_L^n(t_r)}{F_L'(t_r)} \frac{1}{(t-t_r)^2} + \left[\frac{R_L^m R_L^n}{F_L'} \right]_{(t_r)}' \frac{1}{t-t_r} \right\} \quad (\text{Eq B58})$$

where:

$$\left[\frac{R_L^m R_L^n}{F_L'} \right]_{(t_r)}' \equiv \frac{d}{dt} \frac{R_L^m(t)R_L^n(t)}{F_L'(t)} \Big|_{t=t_r} \quad (\text{Eq B59})$$

Equations B45, B46, and B47 are now written as:

$$\int dZ G_{00}(Z) = \frac{b}{b_1} \sum_{r=1}^M \frac{R_L^0(t_r)}{F_L'(t_r)} (I[1, t_r] + I[-1, t_r]) \quad (\text{Eq B60})$$

$$\int dZ b_1 G_{01}(Z) = b \sum_{r=1}^M \frac{R_L^1(t_r)}{F_L'(t_r)} (I[2, t_r] + I[0, t_r]) \quad (\text{Eq B61})$$

and

$$\int dZ G_{0m}(Z) G_{n0}(Z) = \frac{b}{b_1^2} \sum_{r=1}^M \frac{1}{F_L'(t_r)}$$

$$\left\{ \frac{R_L^m(t_r)R_L^n(t_r)}{F_L'(t_r)} (J[m+n+2, t_r] + J[m+n, t_r]) + \left[\frac{R_L^m R_L^n}{F_L'} \right]_{(t_r)}' (I[m+n+2, t_r] + I[m+n, t_r]) \right\} \quad (\text{Eq B62})$$

Integrals have been reduced to some elementary integrals:

$$I[n, s] = \int \frac{t^n}{t-s} dt \quad (\text{Eq B63})$$

$$J[n, s] = \int \frac{t^n}{(t-s)^2} dt = \frac{\partial}{\partial s} I[n, s] \quad (\text{Eq B64})$$

We easily find the following:

$$I[n, 0] = \begin{cases} t^n/n (n \neq 0) \\ \log t (n = 0) \end{cases} \quad (\text{Eq B65})$$

$$J[n, 0] = I[n-1, 0] \quad (\text{Eq B66})$$

$$I[0, s] = \log(t-s) \quad (\text{Eq B67})$$

and

$$J[0, s] = -(t-s)^{-1} \quad (\text{Eq B68})$$

For general n and s we can reduce it to the above cases using recurrence:

$$I[n, s] = I[n, 0] + sI[n-1, s] \quad (\text{Eq B69})$$

and

$$J[n, s] = I[n-1, s] + sJ[n-1, s] \quad (\text{Eq B70})$$

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