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The supersymmetric approach to pseudopotentials in condensed matter physics

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Abstract. The method of supersymmetric transformation is used to obtain from the original true potential V_t the shallower and gentler pseudopotential V^{pp} for the higher (conduction) band by transforming away the levels in the lower core bands. However, it is shown that only after the removal of entire bands will the resulting V^{pp} give rise to smooth, nodeless and essentially norm-conserving pseudowavefunctions. Once a V_t and a few of its lowest core wavefunctions derivable from some self-consistent density functional theory are known, this method of code of constructing V^{pp} should be immediately applicable.

In the calculation of electronic band structures, energetics and other properties including bonding etc the method of pseudopotentials is widely used [1]. This method exploits the orthogonality of the valence electrons in the conduction band to the deeper-lying core states in the lower bands, the requirement of which produces a large kinetic energy that contributes an effective repulsive potential for the valence electrons [2]. In the modern versions of the pseudopotential usually generated from all-electron atomic calculations [1], a spherical screening approximation imposed on the radial Kohn–Sham equation [3] is used to solve for the self-consistent one-electron potential $V[\rho; r]$, $\rho(r)$ being the sum of electron densities for the occupied wavefunctions $R_{nl}(r)$. Most pseudopotentials are then constructed from the above $V[\rho; r]$ by imposing a few general conditions on the corresponding pseudowavefunctions, such as nodelessness, smoothness and norm-conservation [4–10]. In fact, a pseudowavefunction is first constructed by fulfilling those conditions; the remaining non-uniqueness is then exploited to produce a smooth pseudopotential by inverting the radial Schrödinger equation. A cut-off radius r_{cl} is usually chosen [11] so that beyond this radius the normalized atomic radial pseudowavefunction with angular momentum l is equal to the corresponding radial all-electron wavefunction. The screening from the valence electrons has then to be unscreened to retrieve the semilocal ionic pseudopotential that depends on the angular momentum l but is otherwise local [12]. The ionic pseudopotential so obtained is supposedly independent of the chemical environment, i.e. it would adequately reproduce the all-electron behaviour outside the core region when placed in different chemical environments. A local (l-independent) pseudopotential can be extracted from the sum of the semi-local (l-dependent) ones [10] or the semi-local ones can be converted to fully non-local pseudopotentials if so desired for ease of computation in reciprocal space [13].

In this paper we introduce a new approach [14] to the pseudopotential, based not on the concept of orthogonalized plane waves but rather on the recently introduced method of supersymmetric transformation (MST) [15–18]. Once the atomic, screened $V[\rho; r]$ and the associated single-electron ground and low-lying core states of the density functional

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theory, usually obtained by using trial wavefunctions, are known as in the conventional approach, we would be able to construct directly the screened semi-local pseudopotential by applying the MST without having to resort to first constructing a trial pseudowavefunction and then inverting the radial Schrödinger equation. There is then also no need to choose a 'core' radius r_{cl} as mentioned before [11]. The rest of the procedure, such as unscreening and local potential extraction, remains the same as in the conventional approach mentioned above. Aside from guaranteeing the equality of the pseudopotential energy eigenvalues to the valence all-electron energy eigenvalues, our pseudopotential can also be shown to be norm-conserving, thus keeping its significance in calculating energetics, bonding etc intact. In the usual 'core' region, our pseudowavefunctions are automatically nodeless and smooth as naturally follows from the MST without any extra effort. It should then be easy to combine our pseudopotential with plane waves in numerical calculations [10].

To establish the language we shall outline the MST in the context of non-relativistic quantum mechanics as follows [15, 16]. The MST consists in factorizing a Hamiltonian designated as H_1 into two factors in the manner $H_1 = A_1^+A_1^- + E_0$, and in constructing its partner Hamiltonian H_2, $H_2 = A_1^-A_1^+ + E_0$. Here E_0 is the ground state energy of H_1 associated with the eigenfunction $\psi_1^{(0)}(E_0; x)$ and $A^{\pm}(E_0)$ are Hermitian conjugate operators satisfying also the relation that $A^- = (A^+)^\dagger$.

It can be easily shown that if E_n is the nth energy level of H_1 corresponding to the normalized eigenfunction $\psi_1^{(n)}(E_n; x)$, it will also be the $(n-1)$th energy level of H_2 corresponding to the normalized eigenfunction

$$\psi_2^{(n-1)}(E_n; x) = \frac{1}{\sqrt{E_n - E_0}} A_1^-(E_0)\psi_1^{(n)}(E_n; x) \tag{1}$$

except for $n = 0$, in which case $A_1^-(E_0)\psi_1^{(0)}(E_0; x) = 0$ and $\psi_2^{(0-1)}(E_0; x)$ does not exist. This means that the supersymmetric partner H_2 has the same energy spectrum as that of H_1, except for the lowest level E_0 which has been eliminated. The energy E_1 becomes the ground level of H_2. Likewise we can perform a supersymmetric transformation (ST) to

$$H_2 = A_2^+(E_1)A_2^-(E_1) + E_1$$

and find its partner

$$H_3 = A_2^-(E_1)A_2^+(E_1) + E_1$$

whose spectrum is the same as that of H_2 except for E_1, the ground level of H_2, since

$$\psi_3^{(-1)}(E_1; x) \propto A_2^-(E_1)\psi_2^{(0)}(E_1; x) = 0.$$

It is seen that as successive STs are performed, the Hamiltonian changes from H_1 to H_2 and from H_2 to H_3 etc during which the lowest energy levels E_0, E_1 etc are eliminated one by one, respectively. It only remains to find the operators $A_n^{\pm}(E)$, which can be shown to be given by

$$A_n^{\pm}(E) = (1/\sqrt{2})(\pm \mathrm{i}p + U_n(E; x))$$

where $p = -\mathrm{i}\,\mathrm{d}/\mathrm{d}x$. The function $U_n(E; x)$ has to be real and is given by

$$U_n(E; x) = (\mathrm{d}/\mathrm{d}x)\ln\psi_n(E; x)$$

where $\psi_n(E; x)$ satisfies

$$H_n\psi_n(E; x) = E\psi_n(E; x)$$

and the subscript n refers to the stage on the ST ladder. Since

$$H_{n+1} = A_n^-A_n^+ + E = H_n + \Delta V_{n+1} = -\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V_{n+1} \tag{2}$$

the evaluation of the added potential ΔV_{n+1} given by

$$\Delta V_{n+1} = [A_n^-(E), A_n^+(E)] = -\frac{\mathrm{d}^2}{\mathrm{d}x^2}\ln\psi_n(E;x) \tag{3}$$

completes this short outline of the MST, showing the relation between the Hamiltonian H_n and the next one H_{n+1} after one more ST. It is important to note that, for U_n to be real, the eigenfunction ψ_n must necessarily be real for the straightforward application of the ST.

The steps of adapting the MST to finding the pseudopotential V^{pp} is clear. To obtain V^{pp} for a certain energy band, say the conduction band, we just have to transform away all the energy levels below it, one after the other. The potential term in the Hamiltonian after the last ST would then be the V^{pp} we are looking for. This would be, however, an almost impossible task since there are $\sim 10^{22}$ levels in a band. So, one might appeal to the Bloch form of the electron wavefunction and try to deal directly, as usual, with the periodic part $u_{\gamma,k}(r)$ in a unit cell, but the straightforward application of ST to $u_{\gamma,k}(r)$ or to the full Bloch function $\psi_{\gamma,k}(r)$ itself runs into difficulty since neither of them are real, except for the particular values of k such as $k = 0$, for which the wavefunctions represent standing waves [14].

To avoid complex wavefunctions we relax the requirement of the periodic boundary condition by considering a bounded crystal, whose eigenfunctions can be all real. For concreteness and convenience in notations, we may think of a finite Kronig–Penney chain [19].

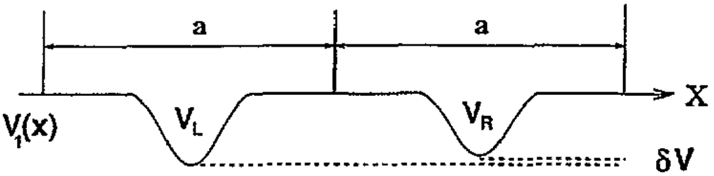

Figure 1. Schematic drawing of the two-well system, showing $V_1 = V_{\mathrm{L}}(x) + V_{\mathrm{R}}(x)$ and the artificially introduced $\delta V \sim 0$.

To demonstrate the removal of an entire band of energy levels it is then sufficient to consider just a few identical potential wells, the simplest case being that of two wells $V_1(x) = V_{\mathrm{L}}(x) + V_{\mathrm{R}}(x)$, depicted in figure 1, which shows two attractive core regions and the flat barrier in between and outside the cores. When the distance between the two slightly dissimilar wells ($\delta V \sim 0$) is very large, the two lowest eigenstates of $H_1 = -\frac{1}{2}\mathrm{d}^2/\mathrm{d}x^2 + V_1(x)$ designated by $\phi_1^{(0)}(\epsilon_{\mathrm{L}}; x) \equiv \phi_{\mathrm{L}}(x)$, $\phi_1^{(1)}(\epsilon_{\mathrm{R}}; x) \equiv \phi_{\mathrm{R}}(x)$ are just the uncoupled ground states of the individual wells on the left and on the right, $V_{\mathrm{L}}(x)$, $V_{\mathrm{R}}(x)$ respectively. An infinitesimally small δV is artificially introduced to make the unperturbed eigenvalues of the two wells slightly different. As the spacing a decreases, coupling occurs and the two corresponding eigenstates of energies E_0 and E_1 are, in the tight-binding approximation, linear combinations of $\phi_{\mathrm{L}}(x)$ and $\phi_{\mathrm{R}}(x)$, given by

$$\begin{pmatrix} \psi_1^{(0)} \\ \psi_1^{(1)} \end{pmatrix} = \begin{pmatrix} C_{0\mathrm{L}} & C_{0\mathrm{R}} \\ C_{1\mathrm{L}} & C_{1\mathrm{R}} \end{pmatrix} \begin{pmatrix} \phi_{\mathrm{L}} \\ \phi_{\mathrm{R}} \end{pmatrix} \tag{4}$$

where the matrix $\mathbf{C}$ has a non-vanishing determinant. Eliminating $\psi_1^{(0)}(E_0; x)$ via the ST, i.e. $A_1^-(E_0)\psi_1^{(0)}(E_0; x) = 0$ as discussed after equation (1), we obtain $H_2 = -\frac{1}{2}\mathrm{d}^2/\mathrm{d}x^2 + V_2(x)$ where $V_2(x) = V_1(x) - (\mathrm{d}^2/\mathrm{d}x^2)\ln\psi_1^{(0)}(x)$ according to equation (3). One can be easily convinced that in $V_2(x)$, while the bottoms of the two wells would rise, the flat inter-well barrier region would become depressed, represented schematically in figure 2. It is seen that the pseudopotential $V_2(x)$ is generally shallower and more gently varying than $V_1(x)$, yet remaining a local potential in this one-dimensional system. However, the ground state wavefunction of this $V_2(x)$ behaves quite differently from $\psi_1^{(1)}(E_1;x)$ in the originally flat inter-well region of $V_1(x)$, i.e. the pseudopotential at this stage of the ST is not norm-conserving. Next we apply the ST once more, eliminating the ground state

$$\psi_2^{(0)}(E_1;x) = [1/\sqrt{(E_1 - E_0)}]A_1^-(E_0;x)\psi_1^{(1)}(E_1;x)$$

of H_2 *via the use of*

$$A_2^-(E_1) = (1/\sqrt{2})[-\mathrm{d}/\mathrm{d}x + (\mathrm{d}/\mathrm{d}x)\ln\psi_2^{(0)}(E_1;x)]$$

that results in $A_2^-(E_1)\psi_2^{(0)}(E_1;x) = 0$. This second ST leaves us with $H_3 = -\frac{1}{2}\mathrm{d}^2/\mathrm{d}x^2 + V_3(x)$ where, by equation (3),

$$V_3(x) = V_2(x) - (\mathrm{d}^2/\mathrm{d}x^2)\ln\psi_2^{(0)}(E_1;x)$$

and the two lowest levels of V_1 of the two-well system have been eliminated.

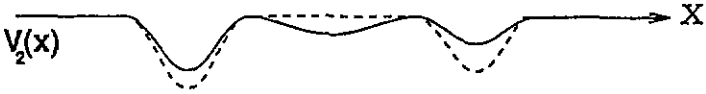

Figure 2. Schematic drawing depicting $V_2(x)$, obtained from $V_1(x)$, about one supersymmetric transformation. Note the depression in the inter-well region.

By the repeated use of equation (3) and equation (1) we can express V_3 in terms of the original V_1 and the two lowest eigenfunctions, $\psi_1^{(0)}$ and $\psi_1^{(1)}$,

$$V_3(x) = V_1(x) - \frac{\mathrm{d}^2}{\mathrm{d}x^2}\ln[-\psi_1^{(0)}\psi_1^{(1)\prime} + \psi_1^{(1)}\psi_1^{(0)\prime}] \tag{5}$$

in which the finite normalization constant $(E_1 - E_0)^{-1/2}$ has disappeared after the spatial differentiations. The prime denotes taking the first spatial derivative.

Expressing $\psi_1^{(0)}$ *and* $\psi_1^{(1)}$ *in terms of* ϕ_L *and* ϕ_R *of the separated wells* V_L *and* V_R via equation (4), and making use of the relation that the argument of the logarithmic term in equation (5) can be written then as

$$\begin{vmatrix} \psi_1^{(0)} & \psi_1^{(1)} \\ \psi_1^{(0)\prime} & \psi_1^{(1)\prime} \end{vmatrix} = \begin{vmatrix} \phi_\mathrm{L} & \phi_\mathrm{R} \\ \phi_\mathrm{L}' & \phi_\mathrm{R}' \end{vmatrix} \begin{vmatrix} C_{0\mathrm{L}} & C_{1\mathrm{L}} \\ C_{0\mathrm{R}} & C_{1\mathrm{R}} \end{vmatrix} \tag{6}$$

we immediately see that, as long as the constant determinant $|\mathbf{C}| \neq 0$, its vanishing upon the spatial differentiation in equation (5) yields the pseudopotential

$$V_3(x) = V_1(x) - \frac{\mathrm{d}^2}{\mathrm{d}x^2}\ln[\phi_\mathrm{R}(x)\phi_\mathrm{L}'(x) - \phi_\mathrm{L}(x)\phi_\mathrm{R}'(x)]. \tag{7}$$

In the spatial region pertaining to the core of V_L, $\phi_\mathrm{L}(x)$ is an oscillating function whose derivative could be roughly estimated as $\phi_\mathrm{L}'(x) \sim k_\mathrm{L}\phi_\mathrm{L}(x)$ where $k_\mathrm{L}^2 = (2m/\hbar^2)(\epsilon_\mathrm{L} + V_0)$. On the other hand, $\phi_\mathrm{R}(x)$ decays fast in this same region which, as far as the corresponding individual $V_\mathrm{R}(x)$ is concerned, is that of the flat, high potential barrier beyond its central attractive core, leading thus to $(\mathrm{d}/\mathrm{d}x)\phi_\mathrm{R} \simeq \tilde{k}_\mathrm{R}(x)\phi_\mathrm{R}$, where $\tilde{k}_\mathrm{R}^2 = -(2m/\hbar^2)\epsilon_\mathrm{R}$. Obviously, for low-lying states in deep wells we have $\tilde{k}_\mathrm{R} \gg k_\mathrm{L}$ because $-\epsilon_\mathrm{L} \simeq -\epsilon_\mathrm{R} \leqslant V_0$. A similar inequality $\tilde{k}_\mathrm{L} \gg k_\mathrm{R}$ holds in the spatial region pertaining to V_R, where ϕ_R oscillates with the wavevector k_R while ϕ_L decays with $\tilde{k}_\mathrm{L}$. It follows that

$$[\phi_\mathrm{R}\phi_\mathrm{L}' - \phi_\mathrm{L}\phi_\mathrm{R}'] \simeq -\tilde{k}\phi_\mathrm{L}\phi_\mathrm{R} \tag{8}$$

in both regions, where $\tilde{k}_{\mathrm{L}} = \tilde{k}_{\mathrm{R}} \equiv \tilde{k} \neq 0$ as $\delta V \to 0$. Since $-(\mathrm{d}^2/\mathrm{d}x^2)\ln\tilde{k} = 0$, equation (7) becomes, in the tight-binding approximation,

$$V_3(x) = V_1(x) - \frac{\mathrm{d}^2}{\mathrm{d}x^2}\ln\phi_{\mathrm{L}}(x) - \frac{\mathrm{d}^2}{\mathrm{d}x^2}\ln\phi_{\mathrm{R}}(x) \tag{9}$$

which is depicted schematically in figure 3.

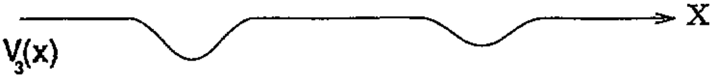

Figure 3. The pseudopotential obtained after two STS, $V_3(x)$, is depicted. Note that while the two attractive cores have become shallower, the flat barrier regions of $V_1(x)$ are also restored.

The exact generalization of the above to the case of N equally spaced potential wells, though non-trivial, can be made. For example, in the case of three wells labelled as 1, 2 and 3, the determinant of equation (6) is generalized, in obvious notations, to

$$\begin{vmatrix} \psi_1^{(0)} & \psi_1^{(1)} & \psi_1^{(2)} \\ \psi_1^{(0)\prime} & \psi_1^{(1)\prime} & \psi_1^{(2)\prime} \\ \psi_1^{(0)\prime\prime} & \psi_1^{(1)\prime\prime} & \psi_1^{(2)\prime\prime} \end{vmatrix} \simeq \begin{vmatrix} \phi_1 & \phi_2 & \phi_3 \\ \phi_1' & \phi_2' & \phi_3' \\ \phi_1'' & \phi_2'' & \phi_3'' \end{vmatrix} \begin{vmatrix} C_{01} & C_{11} & C_{21} \\ C_{02} & C_{12} & C_{22} \\ C_{03} & C_{13} & C_{23} \end{vmatrix} \tag{10}$$

where the ϕ_i are the atomic-like states in the separated wells and the $\psi_1^{(n)}$ are the tight-binding eigenfunctions of the nth energy level of the three-well Hamiltonian. The determinant $|\mathbf{C}|$ is that of the coefficients in the linear combinations of the ϕ_i in forming the $\psi_1^{(n)}$.

In the spatial region of potential well 1, say, we may neglect ϕ_1' and ϕ_1'' in comparison to the derivatives of ϕ_2 and ϕ_3 in the tight-binding approximation. The determinant of the ϕ_i in equation (10) can then be approximated as $\phi_1(x)[(\tilde{k}_2\tilde{k}_3^2 - \tilde{k}_3\tilde{k}_2^2)\phi_2(x)\phi_3(x)]$ where $\tilde{k}_2$, $\tilde{k}_3$ are the large decay constants of ϕ_2 and ϕ_3 in region 1. Due to the artifice of introducing the δV to distinguish the wells V_i from each other, $\tilde{k}_2$ and $\tilde{k}_3$ are only nearly but not exactly equal to each other, leading thus to $(\mathrm{d}^2/\mathrm{d}x^2)\ln(\tilde{k}_2\tilde{k}_3^2 - \tilde{k}_3\tilde{k}_2^2) = 0$.

It then follows, as in the steps leading to equation (9), that, after three successive supersymmetric transformations to eliminate the tight-binding band of the three lowest levels in the three-well system [20], the resulting pseudopotential is given by

$$V_4(x) = V_1(x) - \sum_{n=1}^{3}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\ln\phi_n(x). \tag{11}$$

It is now clear that, for N wells, the pseudopotential after the elimination of the band of the N lowest levels is

$$V_{N+1} = V_1(x) - \sum_{n=1}^{N}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\ln\phi_n(x) \tag{12}$$

where $\phi_n(x)$ is the ground state of the nth individual, atomic-like potential well. The combination of N such wells form V_1, the starting crystal potential on our ST ladder derivable from, say, density functional theory [1, 3].

In the special case of $N = 1$, equation (12) yields the single-well pseudopotential for an atomic-like system after the elimination of its lowest core states. For an arbitrary, large N, the pseudopotential obtained after transforming away the first M levels, with $M < N$, is generally extremely complicated, as could be extrapolated from figure 2. It is only after eliminating the whole band of N levels, whose wavefunctions are assumed to be linear combinations [21] of the $\phi_n(x)$, that the simple form of the pseudopotential as in equation (12) emerges. It obviously represents again a lattice of N wells, but each now modified into a single-well pseudopotential given by the $N = 1$ case.

A simpler mathematical proof can now be provided. Let ψ_i denote the ith bound eigenstate of any Hamiltonian H. We can eliminate such states by applying the operators A_i according to the SST, i.e., $A_1\psi_1 = 0$, $A_2A_1\psi_2 = 0$, $A_n \ldots A_2A_1\psi_n = 0$. For any linear combinations of ψ_i such as the ϕ_i for the individual ith well given by $\phi_i = C_{i1}\psi_1 + C_{i2}\psi_2 + \ldots + C_{iN}\psi_N$, if we apply $A_N \ldots A_2A_1$ to ϕ_i, it always gives zero, i.e. $A_N \ldots A_2A_1\phi_i = 0$. Hence, eliminating all the ψ_i with $i = 1, 2, \ldots, N$ by applying $A_N, \ldots, A_2, A_1$, would be equivalent to eliminating all the ϕ_i for the individual well $1, 2, \ldots, N$, and vice versa. This proof is clearly valid not only for one dimension, but also for any number of dimensions. The physical reason behind this is clear. When we eliminate the lowest core level from each individual well, the tight-binding band, whose wavefunctions are constructed by linearly combining just those single-well core wavefunctions, is naturally also eliminated as a whole. The converse is also true, of course. The validity of this physical reasoning again extends beyond one dimension, enabling us also to conclude that equation (12) holds for any number of dimensions. This relation between the individual wells and the lattice potential is implied in the conventional approach to the pseudopotential. However, it has to be proved explicitly as a price to pay for adapting the MST to the construction of the pseudopotential. Nevertheless, our gain is considerable.

First, the pseudopotential in equation (12) is explicitly local.

Second, the pseudowavefunction for the valence electron, being the ground wavefunction in each modified (by ST) pseudopotential well, is automatically nodeless everywhere, including the original 'core' regions, although no core radius needs to be specified.

Third, wherever the true potential is flat or mildly varying, our pseudopotential of equation (12) will remain that way (see figure 3) since $-\sum_{n=1}^{N}(\mathrm{d}^2/\mathrm{d}x^2)\ln\phi_n(x)$ becomes vanishingly small due to the pure exponential decay form of the $\phi_n(x)$ there. Each valence electron pseudowavefunction $\psi_k(E_k; x)$ will then be a linear combination of two terms, one exponentially decaying, the other growing in these flat barrier regions asymptotically. The ratio and the relative phase of the two associated amplitudes are fixed once the decay and growth constants $\pm Q$ and the Bloch momentum k are specified [22]. Since Q is, in turn, determined by the height of the flat barrier above the eigenenergy E_k, neither of which is changed by the STs, the ratio of the two amplitudes including the relative phase, and hence the wavefunction $\psi_k(E_k; x)$ itself, remain the same in these flat regions under the multiple STs that result in the pseudopotential of equation (12). This means that our pseudopotential is norm-conserving for a wavefunction of any given Bloch momentum k and energy E_k above the core bands.

Fourth, the valence electron pseudowavefunctions are solved only after the semi-local pseudopotential of equation (12) has been found. There is no need to invert a radial Schrödinger equation constructed for trial pseudowavefunctions.

One further clarification for the construction of pseudopotentials in three dimensions is in order. For a three-dimensional solid with N atomic potential wells (muffin-tin shaped, say) that together make up the crystalline potential $V(\boldsymbol{r})$, if ϕ_i denotes a certain *atomic* core level, we could merely transform away this *atomic* level from each of the N atomic potential wells, and the result would be the elimination of the whole core band of *crystalline* energy levels formed by linear combinations of the above N atomic wavefunctions. The key question left is: can we transform away this ϕ_i corresponding to a wavefunction for the three-dimensional atom, in view of the fact that our supersymmetric transformation equations (1)–(3) are valid only for one dimension? The answer is obviously yes. This is because, under the usual spherical screening approximation [3], each single atomic potential is isotropic, leading to the conservation of angular momentum. Each atomic eigenfunction is therefore a product of a spherical harmonic (complex in general) and a radial wavefunction. The Schrödinger equation for the radial part is, of course, real. For any given angular momentum l, there are correspondingly various real radial wavefunctions and energy eigenvalues. Since this radial Schrödinger equation is one dimensional, we can readily apply the supersymmetric transformation to eliminate the core levels associated with the radial wavefunctions one by one. For example, the transforming away of, say, a 3s atomic level, is equivalent to transforming away the whole 3s band of the crystalline solid. Thus, in three dimensions our psuedopotential for each individual well of equation (12) will, in the spherical screening approximation [3], depend on the angular momentum l of the atomic radial pseudowavefunction. In this sense, our psuedopotential is semi-local [12].

In conclusion, we have substantiated our claims made in the introductory paragraphs and shown that the MST constitutes a new and simpler approach to the construction of semi-local pseudopotentials.

Acknowledgments

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[20] The artificial δV, which may be thought of as simulating the ever-present lattice imperfections, can be taken to be zero at the end of the calculation.

[21] In cases when semi-core levels are also involved as for transition metals, the tight binding has to be relaxed to include more than one core level in the linear combinations, but the MST can be easily generalized correspondingly.

[22] That this is so can be explicitly verified in the Kronig–Penney model. In the notations of pp 164–5 of [19], the ratio of the two amplitudes, C/D, depends on Q, k and K. The eigenenergy parametrized by K can, in turn, be solved from the Schrödinger equation in terms of Q and k, with no further dependence on

the well depth U_0. This means that C/D can be uniquely determined independently of the well depth which might change upon ST, once Q and k are specified. In the case of $k = 0$ when the Bloch function $\psi(k, x)$ itself becomes periodic over the atomic-like unit cells of the entire chain, the ratio C/D is given by $\exp(Qb)$, explicitly independent of the shape of the attractive core potential.