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## Localized Symmetry-Adapted Perturbation Theory and a New Tight-Binding Expansion

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A new symmetry-adapted perturbation theory is suggested with the following improved properties: The primitive function is localized, and for Coulomb potentials has only a single cusp; the modified equation has no spurious bound states. A systematic tight-binding perturbation expansion involving only two-center integrals is derived.

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In many branches of physics complex systems are described as consisting of simpler "building blocks," e.g., a molecule or a solid may be treated as built up of single atoms or "cells." In the case of a small overlap between neighboring cells' wave functions, approximations of successively increasing order may be constructed starting from "atomic" orbitals. In the present Letter we develop an approach to such problems using a new formulation of a method used in quantum chemistry<sup>1,2</sup> and in nuclear physics<sup>3</sup> under the names of symmetry-adapted perturbation theory (SAPT) and perturbation theory for projected states, respectively. SAPT is used when the complex system possesses some symmetry (e.g., reflections, translations, identical-particle interchange, etc.). Let  $P$  be a projection operator ( $P^2=P$ ,  $P^\dagger=P$ ) onto some representation of the symmetry group of  $H$ , where  $H$  is the Hamiltonian of the complex system. We have  $[P,H]=0$ , with  $H=T+U$ , where  $T$  and  $U$  are the kinetic and the

potential energy operators. The complex system wave function  $\psi$  ( $H\psi=E\psi$ ,  $P\psi=\psi$ ) cannot usually be approximated by the solution  $\varphi_0$  of an "atomic" problem,  $H_0\varphi_0=E_0\varphi_0$ ,  $H_0=T+V_0$ , where  $V_0$  is an atomic potential. Rather, one needs all the atomic orbitals which are obtained by applying to  $\varphi_0$  the operations of the symmetry group of  $H$ . In SAPT a modified equation is introduced,<sup>1-4</sup> for a "primitive function"  $\varphi$ ,

$$(H-E)\varphi=(1-P)F(E,\varphi); \quad (1)$$

$\varphi_0$  is expected to be a good approximation to  $\varphi$ , and  $\psi$  is obtained from  $\varphi$  by projection ( $\psi\propto P\varphi$ ). There is an extensive literature<sup>1-3,5</sup> on the optimal choice of the functional  $F(E,\varphi)$ , so that higher-order corrections to  $\varphi_0$  may be treated by perturbation theory.

The wave function  $\psi$  is extended over the whole system, whereas atomic orbitals are centered on particular atoms. The requirement that  $\varphi$  of Eq. (1) be localized, similarly to  $\varphi_0$ , is an obvious

condition on the choice of  $F(E, \varphi)$ . This problem was studied previously in several works,<sup>5,6</sup> with different definitions of a "localized function." In molecular and solid-state calculations  $\psi$  usually has "cusps" at atomic centers, due to Coulomb potentials. A natural condition on the optimal  $\varphi$  [Eq. (1)] is that it should have only a single cusp; to our best knowledge, this question has not been studied systematically in SAPT.<sup>7</sup>

We suggest a new formalism with the following improved properties:  $\varphi$  is exponentially localized and may be chosen to have a single cusp. We prove a one-to-one correspondence between the bound-state spectrum of the modified equation and the original equation ( $H\psi = E\psi$ ).<sup>8</sup> The localization and single-cusp properties of  $\varphi$  improve the convergence of approximation methods. After introducing the general formalism, we mention briefly possible applications and consider in more detail the tight-binding approximation for Bloch states in solids, constructing a perturbation expansion for this case. The improved convergence properties of this new expansion are studied in a solvable Kronig-Penney model.

Let  $Q_1, Q_2, \dots, Q_g$  denote the operations of the symmetry group of  $H$ , with  $Q_1 \equiv 1$ . Note first that the *spatial* symmetry operations (reflections, translations, identical-particle interchange) act separately on the factors of a product:  $Q_i(f_1 f_2) = (Q_i f_1)(Q_i f_2)$ ,  $Q_i(f_1/f_2) = (Q_i f_1)/(Q_i f_2)$  {e.g., for reflection symmetry:  $g=2$ ,  $Q_2=R$ , and the first equation reads  $R[f_1(x)f_2(x)] = f_1(-x)f_2(-x)$ }. Any spatial symmetry commutes with the kinetic energy  $T$ , and therefore  $[Q_i, H] = [Q_i, T] = [Q_i, U] = 0$ . For a specific one-dimensional representation, the projector  $P$  is of the form<sup>9</sup>

$$P = \frac{1}{g} \sum_{n=1}^g q_n^* Q_n,$$

where the characters  $q_i$  satisfy  $|q_i|^2 = 1$ . We start with the modified equation in the form

$$H'\varphi = E\varphi, \quad \text{with } H' = T + SU, \quad (2)$$

where the operator  $S$  satisfies<sup>3</sup>  $PS = P$  and  $SP = S$ .<sup>10</sup> Specific choices of  $S$  will be discussed later in connection with localizing  $\varphi$ . Note that Eq. (2) reduces to Eq. (1) for  $F \equiv (1-S)U\varphi$ . Applying  $P$  to  $H'\varphi = E\varphi$  we get  $H(P\varphi) = E(P\varphi)$ ;  $P\varphi$  is the desired solution ( $\psi \propto P\varphi$ ), unless  $P\varphi = 0$  (a spurious solution<sup>8</sup>). However, assuming  $P\varphi = 0$ , we get  $SU\varphi = SP(U\varphi) = SUP\varphi = 0$ , and Eq. (2) reduces to  $T\varphi = E\varphi$ . The last equation has no bound ( $E < 0$ ) states, and therefore Eq. (2) has no spurious bound states.<sup>11</sup> Conversely, for a given

bound state  $\psi$  of the proper symmetry ( $P\psi = \psi$ ) there exists a corresponding solution  $\varphi$  of Eq. (2). Indeed,  $\varphi \propto (E - T)^{-1}SU\psi$ , as can be verified by direct substitution. The above property of the spectrum of Eq. (2) was not established for other formulations of SAPT.

In order to localize bound-state solutions of the modified equation, we choose

$$S = \frac{l}{L}P, \quad \text{with } L = \frac{1}{g} \sum_{n=1}^g (Q_n l), \quad (3)$$

where the localizing function  $l$  is chosen so that it decays outside a single cell similarly to the atomic potential;  $L$  is a completely symmetric projection of  $l$ . The condition  $SP = S$  is trivially satisfied; let us check whether  $PS = P$ :

$$\begin{aligned} PS &= \frac{1}{gL} \sum_i q_i^* Q_i (lP) \\ &= \frac{1}{gL} \sum_i q_i^* (Q_i l) q_i P = \left( \frac{1}{gL} \right) gLP = P. \end{aligned}$$

The modified equation reads

$$[T + (l/L)UP - E]\varphi = 0, \quad (4)$$

and localization of  $\varphi$  arises similarly to the usual Schrödinger equation: the "potential" term  $(l/L)UP\varphi$  decays outside a single cell (because of the presence of  $l$ ). Thus bound states of Eq. (4) decay exponentially.

The potential energy  $U$  is completely symmetric and may be represented as a projection,  $U = \sum_i Q_i \times V Q_i^\dagger$ . Usually, there is a natural choice:  $V \equiv V_0$  in a problem. Choosing  $l \equiv V_0$  we get<sup>12</sup>

$$(T + gV_0P - E)\varphi = 0. \quad (5)$$

Consider, for example, the  $H_2^+$  ion, with two fixed nuclei at  $\pm a\hat{x}$ :  $H = T - e^2/|\vec{r} - a\hat{x}| - e^2/|\vec{r} + a\hat{x}|$ . The natural choice of  $V_0$  is  $V_0 = -e^2/|\vec{r} - a\hat{x}|$ . We get

$$\begin{aligned} H' &= T - (e^2/|\vec{r} - a\hat{x}|)(1 + q_2R) \\ &= T + V_0 + q_2V_0R, \end{aligned} \quad (6)$$

where  $q_2 = +1$  ( $-1$ ) for positive- (negative-) parity states. For a large separation  $2a$ ,  $\varphi$  is localized at  $+a\hat{x}$ , and  $H'$  is a single-center operator with a Coulomb term at  $+a\hat{x}$  only. The overlap part in the equation  $H'\varphi = E\varphi$  is  $q_2V_0R\varphi$ , with  $V_0$  centered at  $+a\hat{x}$ , and  $R\varphi$  at  $-a\hat{x}$ , and may be treated as a perturbation to  $H_0 = T + V_0$ . Improved convergence of perturbation series based on equations of the type of Eq. (6) was studied by the authors.<sup>5</sup>

For intermolecular interactions, the relevant

symmetry is electron exchange.<sup>1,2</sup> Note that a many-electron  $\varphi$  may be localized at different centers for different electronic coordinates [choosing an appropriately localized  $l(\vec{x}_1, \vec{x}_2, \dots)$  in Eq. (4)].

In the following we apply our method to the periodic potential problem (for several other methods of defining and calculating localized atomiclike orbitals in this case, see Refs. 6, 13, and 14). Let  $\vec{R}_n$  denote lattice vectors (with  $\vec{R}_0 = 0$ ); we have  $Q_n f(\vec{x}) = f(\vec{x} - \vec{R}_n)$ ,  $q_n = \exp(-i\vec{k} \cdot \vec{R}_n)$ ,  $g \rightarrow \infty$ , where  $\vec{k}$  labels the representations. The periodic potential  $U(\vec{x})$  is  $U(\vec{x}) = \sum_n V_0(\vec{x} - \vec{R}_n) = \sum_n Q_n V_0(\vec{x}) Q_n^\dagger$ ; the condition  $V_0(\infty) = 0$  determines the zero of energy; in practice, one will

use a solvable atomic-type  $V_0$ . The limit  $g \rightarrow \infty$  is straightforward in Eq. (5), and we obtain

$$[H_0 + V_0(\vec{x}) \sum_{n \neq 0} \exp(i\vec{k} \cdot \vec{R}_n) Q_n - E_{\vec{k}}] \varphi_{\vec{k}} = 0, \quad (7)$$

$$H_0 = T + V_0(\vec{x}).$$

This equation is useful in studying the lowest "tight-binding" (TB) energy bands which result from broadening of atomic bound states ( $\varphi_0$ ). In this case  $\varphi_{\vec{k}}$  of Eq. (7) is localized at the origin, and for Coulomb potentials has a single cusp.<sup>15</sup> We set up a perturbation expansion,  $E_{\vec{k}} = E_{\vec{k}}^{(0)} + E_{\vec{k}}^{(1)} + \dots$  and  $\varphi_{\vec{k}} = \varphi_{\vec{k}}^{(0)} + \varphi_{\vec{k}}^{(1)} + \dots$ , based on the smallness of matrix elements arising from the terms  $\exp(i\vec{k} \cdot \vec{R}_n) V_0(\vec{x}) Q_n \varphi(\vec{x})$ ,  $n \neq 0$ , in Eq. (7). We have<sup>16</sup>

$$\varphi_{\vec{k}}^{(0)} = \varphi_0, \quad \psi_{\vec{k}}^{(0)} \propto \sum_n \exp(i\vec{k} \cdot \vec{R}_n) \varphi_0(\vec{x} - \vec{R}_n),$$

$$E_{\vec{k}}^{(0)} = E_0, \quad E_{\vec{k}}^{(1)} = \sum_{n \neq 0} \langle \varphi_0(\vec{x}) | V_0(\vec{x}) | \varphi_0(\vec{x} - \vec{R}_n) \rangle \exp(i\vec{k} \cdot \vec{R}_n) / \langle \varphi_0 | \varphi_0 \rangle,$$

etc.  $\psi_{\vec{k}}^{(0)}$  is the usual TB trial wave function;  $E_{\vec{k}}^{(0)} + E_{\vec{k}}^{(1)}$  is compatible in accuracy with the usual TB expectation value (we give an example below). However, note that our  $E_{\vec{k}}^{(1)}$  involves only two-center integrals,<sup>17</sup> and this property holds in all orders of our perturbation expansion, whereas usually in TB calculations three-center integrals appear.<sup>18</sup>

Let us consider a solvable Kronig-Penney model<sup>19</sup>—a one-dimensional attractive  $\delta$ -function "comb." The atomic problem with  $H_0 = -\frac{1}{2} d^2/dx^2 - Z\delta(x)$  has one bound state:  $\varphi_0 = Z^{1/2} e^{-Z|x|}$ ,  $E_0 = -Z^2/2$ . We consider the lowest energy band of

$$H = -\frac{1}{2} \frac{d^2}{dx^2} - Z \sum_{n=-\infty}^{\infty} \delta(x - na)$$

in the TB ( $Za \gg 1$ ) limit. The modified "Hamiltonian" is  $H_k' = -\frac{1}{2} d^2/dx^2 - Z\delta(x) + \Delta H_k$ , where  $\Delta H_k = -Z\delta(x) \sum_{n \neq 0} e^{ikna} Q_n$ . We recall that the second-order energy,  $E_k^{(2)}$ , is given by  $\langle \varphi_0 | \Delta H_k \Gamma \Delta H_k | \varphi_0 \rangle$ , where  $\Gamma$  is the reduced resolvent of  $H_0$ ; in our case the explicit form of the kernel  $\bar{\Gamma}(x, y)$  of  $\Gamma$  is

$$\bar{\Gamma}(x, y) = (|x| + |y| + 1/2Z) \exp(-Z|x| - Z|y|) - (1/Z) \exp(-Z|x - y|).$$

Using the above-listed formulas, we have  $E_k^{(1)} = -Z^2 Y(Za, ka)$ ,

$$E_k^{(2)} = -Z^2 [Y^2/2 + (Za) Y \partial Y(Za, ka) / \partial (Za)],$$

where

$$Y(\alpha, \beta) \equiv 2e^{-\alpha} (\cos \beta - e^{-\alpha}) / (1 - 2e^{-\alpha} \cos \beta + e^{-2\alpha}).$$

The exact bound-state solution of  $H_k' \varphi_k = E_k \varphi_k$  is  $\varphi_k \propto \exp(-\beta_k |x|)$ ,  $E_k = -\beta_k^2/2$ , where  $\beta_k$  is a positive root of  $\beta_k = Z[1 + Y(\beta_k a, ka)]$ . Our method allows the derivation of successively higher-order expansions in terms of parameters which describe the smallness of "overlap" terms. In the Kronig-Penney model the natural expansion parameter is  $e^{-Za}$ ; in fact,

$$E_k/E_0 = 1 + e^{-Za} (4 \cos ka) + e^{-2Za} (12 \cos^2 ka - 8Za \cos^2 ka - 4) + O(e^{-3Za}).$$

Our  $E_k^{(0)} + E_k^{(1)}$  reproduces correctly the first two terms (when expanded in powers of  $e^{-Za}$ );  $E_k^{(0)} + E_k^{(1)} + E_k^{(2)}$  reproduces also the third term. The simple TB expectation value gives only the first two terms correctly; in fact,

$$\langle \psi_k^{(0)} | H | \psi_k^{(0)} \rangle / \langle E_0 | \psi_k^{(0)} | \psi_k^{(0)} \rangle = 1 + e^{-Za} (4 \cos ka) + e^{-2Za} (8 \cos^2 ka - 8Za \cos^2 ka - 4) + O(e^{-3Za}).$$

Thus far we have used the Rayleigh-Schrödinger perturbation series. Consider now the Brillouin-

Wigner perturbation series:  $\varphi_k(x) = \varphi_0 + \sum_{r=1}^{\infty} (\Lambda \Delta H_k)^r \varphi_0 = \varphi_0 + \varphi_k^{(1)} + \varphi_k^{(2)} + \dots$ , where  $\Lambda$  is the reduced resolvent of  $H_0$  calculated at the exact  $E_k$ ; the kernel  $\tilde{\Lambda}(x, y)$  of  $\Lambda$  is known in closed form.<sup>20</sup> One may derive the following result: The  $r$ th term ( $r \geq 1$ ) is

$$\varphi_k^{(r)} = \sqrt{Z} \frac{Y(Za, ka)}{Y(\beta_k a, ka)} \left[ 1 - \frac{2Z}{Z + \beta_k} \frac{Y(Za, ka)}{Y(\beta_k a, ka)} \right]^{r-1} \left( \exp(-\beta_k |x|) \frac{2Z}{Z + \beta_k} e^{-Z|x|} \right). \quad (8)$$

We observe that  $\varphi_k^{(r+1)}/\varphi_k^{(r)}$  is a constant and thus the series converges geometrically if  $|\varphi_k^{(r+1)}/\varphi_k^{(r)}| < 1$ . In the small-overlap limit ( $e^{-Za} \ll 1$ ) we have

$$\varphi_k^{(r+1)}/\varphi_k^{(r)} = (1 - 2Za) \cos ka e^{-Za} + O(e^{-2Za}),$$

and the rate of convergence is related to the smallness of the overlap. Summing the series, we re-derive<sup>21</sup>  $\varphi_k = [(Z + \beta_k)/2\sqrt{Z}] \exp(-\beta_k |x|)$ . The primitive function  $\varphi_k$  is similar to the atomic  $\varphi_0$  [note that  $\beta_k = Z + O(e^{-Za})$ ].

In summary, we have suggested a new SAPT method which employs a primitive function localized similarly to the atomic one. Our method is free of spurious-state problems, and the primitive function has only a single cusp when Coulomb potentials are present. The new method yields a systematic perturbation expansion in which only two-center integrals appear, even if the potential of the complex system is multicentered.

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<sup>1</sup>For reviews and references to original works, see, e.g., P. Claverie, in *Intermolecular Interactions: From Diatomics to Biopolymers*, edited by B. Pullman (Wiley, New York, 1978), Chap. 2; D. M. Chipman, J. D. Bowman, and J. O. Hirschfelder, *J. Chem. Phys.* **59**, 2830 (1973); I. G. Kaplan and O. B. Rodimova, *Usp. Fiz. Nauk* **126**, 403 (1978) [*Sov. Phys. Usp.* **21**, 918 (1978)].

<sup>2</sup>For more recent work and further references, consult C. A. Venanzi, B. Kirtman, and D. M. Chipman, *Phys. Rev. A* **21**, 1443 (1980); B. Jeziorski and W. Kolos, *Comments At. Mol. Phys.* **11**, 45 (1981); W. H. Adams and E. E. Polymeropoulos, *Phys. Rev. A* **17**, 11 (1978); W. Kutzelnigg, *J. Chem. Phys.* **73**, 343 (1980).

<sup>3</sup>R. E. Peierls, *Proc. Roy. Soc. London, Ser. A* **333**, 157 (1973); B. Atalay, A. Mann, and R. E. Peierls, *Proc. Roy. Soc. London, Ser. A* **335**, 251 (1973).

<sup>4</sup>Some of the equations used in the literature (Refs. 1–3) look different, but they usually can be reduced to the form of Eq. (1) with a suitable choice of  $F$ .

<sup>5</sup>A. Mann and V. Privman, *Phys. Lett.* **64A**, 361 (1978); W. Kutzelnigg, *Int. J. Quantum Chem.* **14**, 101 (1978).

<sup>6</sup>D. M. Chipman, *J. Chem. Phys.* **66**, 1830 (1976), and references therein; W. H. Adams, *Phys. Rev. Lett.* **32**, 1093 (1974).

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<sup>8</sup>Spurious solutions, for which  $P\varphi = 0$ , may cause problems in SAPT; See B. I. Atalay, A. Mann, and A. Zelicoff, *Nucl. Phys.* **A295**, 204 (1978); P. Claverie, *Int. J. Quantum Chem.* **5**, 273 (1971).

<sup>9</sup>M. Hamermesh, *Group Theory* (Addison-Wesley, Reading, Mass., 1964), Chap. 4.

<sup>10</sup>These equations have a general solution,  $S = P + (1-P)MP$ , with arbitrary  $M$  [B. Atalay and A. Mann, *Phys. Lett.* **60A**, 269 (1977)]. Operators of this type were first introduced in SAPT by Peierls (see Ref. 3).

<sup>11</sup> $E > 0$  spurious states satisfy  $T\varphi = E\varphi$ ,  $P\varphi = 0$ , and may be easily isolated ( $E \geq 0$  is defined by the requirement that all the atomic potentials in the problem vanish at infinity).

<sup>12</sup>In the case  $g=2$  an equation equivalent to Eq. (5) was derived in Mann and Privman, Ref. 5, using a different method.

<sup>13</sup>For a general overview, consult D. W. Bullett, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1980), Vol. 35, Chap. 2.

<sup>14</sup>P. W. Anderson, *Phys. Rev. Lett.* **21**, 13 (1968), and *Phys. Rev.* **181**, 25 (1969); J. D. Weeks, P. W. Anderson, and A. G. H. Davidson, *J. Chem. Phys.* **58**, 1388 (1973); W. Kohn, *Phys. Rev. B* **7**, 4388 (1973); one version of SAPT for periodic potentials was considered by L. Piela, *J. Phys. C* **8**, 2606 (1975).

<sup>15</sup> $\varphi$  is still singular at other Coulomb centers, but the singularity is weaker: "cusps" in the second derivatives.

<sup>16</sup>We consider for simplicity only the case of nondegenerate atomic  $\varphi_0$ .

<sup>17</sup>We are indebted to Professor J. Zak for pointing out this property to us.

<sup>18</sup>J. L. Fy, N. E. Brener, F. C. Case, and N. L. Desai, *Phys. Rev. B* **15**, 5811 (1977); see also Ref. 13.

<sup>19</sup>R. de L. Kronig and W. Penney, *Proc. Roy. Soc. London* **130**, 499 (1931).

<sup>20</sup>See, e.g., A. Mann and R. E. Peierls, *Chem. Phys. Lett.* **24**, 136 (1974).

<sup>21</sup>The normalization of  $\varphi_k$  is fixed by  $\langle \varphi_0 | \varphi_k \rangle = 1$ .