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Non-local separable potential approach to multicentre interactions

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It is shown that nonlocal separable potentials may be used to study bound states of particles in multicentre potentials. The binding energy is obtained in a closed form. The cases of H_2^+ ion and polymer chains are discussed in detail and results compared to experimental data.

1. Introduction

The solution of the Schrödinger equation for multicentre potentials is of general interest in atomic, molecular and solid state physics. Several methods have been developed to study the motion of an electron in a given superposition of three-dimensional potentials. In particular, the small-radius potential (SRP) approximation has been widely used in different branches of quantum mechanics [1–3]. The SRP approximation, however, is only valid for low-energy particles [4], and we might include information not only about the potential strength but also about the potential shape to obtain more accurate results. The natural way to generalize the SRP approximation is the non-local (separable) potential (NLP) method, in which the actual potential at each site is replaced by a projective operator [5, 6]. This method leads to an exactly solvable Schrödinger equation and the energy of the particle is also obtained in a closed form even for finite-range potentials. What is more important, it is always possible to find a nonlocal separable potential (or a sum of them) which reproduces any set of given particle states [5, 7]. There is, therefore, no theoretical limit to the numerical precision with which physical results may be obtained.

In this paper we investigate the possibility of applying the NLP method to study some problems appearing in molecular physics. We will see that this method affords accurate results for the binding energy of electrons in a rather simple way.

2. The H_2^+ ion

In this case we are faced with a two centre potential. The electron moves under the action of the Coulomb field of two protons separated by a distance R. In the framework of the Born–Oppenheimer approximation we can study the electronic motion treating R as a parameter, hence decoupling the electronic motion from the vibro-rotational molecular behaviour. Although this problem has been extensively analysed and admits exact solutions [8], we wish to present an alternative treatment based on NLP method to illustrate its convenience in situations where exact solutions of the Schrödinger equation are difficult to obtain.

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The Schrödinger equation for NLP we consider in this case reads

$$(\boldsymbol{p}^2 + \kappa^2)\psi(\boldsymbol{r}) = \sum_{i=1}^{2} g_i v_i(|\boldsymbol{r} - \boldsymbol{R}_i|) \int \mathrm{d}^3 r' \, v_i(|\boldsymbol{r}' - \boldsymbol{R}_i|)\psi(\boldsymbol{r}') \tag{1}$$

where $\boldsymbol{R}_i$ denotes the position of each proton and g_i is the corresponding coupling constant. We use spherically symmetric potentials $v_i(r)$ in order to describe the electron ground state. Due to the symmetry of the problem we can write $g_1 = g_2 \equiv g$ and $v_1 = v_2 \equiv v$. In the Fourier transform space we have

$$\psi(\boldsymbol{p}) = g \frac{v(p)}{p^2 + \kappa^2} \sum_{i=1}^{2} \exp(-\mathrm{i}\boldsymbol{p} \cdot \boldsymbol{R}_i)\chi_i, \tag{2}$$

where

$$\chi_i = \int \mathrm{d}^3 p \exp(-\mathrm{i}\boldsymbol{p} \cdot \boldsymbol{R}_i) v^*(p)\psi(\boldsymbol{p}) \tag{3}$$

Here $f(\boldsymbol{p})$ denotes the Fourier transform of the function $f(\boldsymbol{r})$. Inserting (2) in (3) we obtain two algebraic equations for χ_1 and χ_2. We require the determinant to vanish for non-trivial solutions, so that

$$\left(\frac{1}{4\pi g} - P\right)^2 = Q^2 \tag{4}$$

where we have introduced the notation

$$P = \int_0^\infty \mathrm{d}p \frac{p^2|v(p)|^2}{p^2 + \kappa^2}, \tag{5a}$$

$$Q = \int_0^\infty \mathrm{d}p \frac{p^2|v(p)|^2}{p^2 + \kappa^2} \frac{\sin(pR)}{pR} \tag{5b}$$

and $R = |\boldsymbol{R}_1 - \boldsymbol{R}_2|$.

We have found it most appropriate to use the Yamaguchi's NLP [9], which is given in the position representation by $V(r) = (1/r)\exp(-r/\alpha)$, α being the Bohr radius in our case. Notice that the Yamaguchi's potential is simply the Coulomb local potential times the electron ground state wavefunction for this potential. In the Fourier transform space we have

$$v(p) = (2/\pi)^{1/2} \frac{1}{p^2 + \alpha^{-2}} \tag{6}$$

and (5) now reads

$$P = \frac{\alpha^3}{2(1 + \alpha\kappa)^2}, \tag{7a}$$

$$Q = \frac{\alpha^3}{2(\alpha^2\kappa^2 - 1)} \exp(-R/\alpha)\left(1 - 2\frac{1 - \exp[-(R/\alpha)(\alpha\kappa - 1)]}{(R/\alpha)(\alpha\kappa - 1)}\right). \tag{7b}$$

To calculate the coupling constant g we consider the limit $R \to 0$ in (7b). In that situation $Q \to P$ and (4) and (7a) lead to

$$g = (1 + \alpha\kappa)^2/4\pi\alpha^3. \tag{8a}$$

Physically this limit means that we are dealing with the He^+ ion, for which the ground

state energy is $E = -2/m\alpha^2$. Therefore $\kappa = 2/\alpha$ in (8a) and the coupling constant is found to be

$$g = 9/4\pi\alpha^3. \tag{8b}$$

For any arbitrary separation R, (4) may be written as

$$1 - \frac{9/2}{(1+\alpha\kappa)^2} = \frac{(9/2)\exp(-R/\alpha)}{2(\alpha^2\kappa^2-1)}\left(1 - 2\frac{1-\exp[-(R/\alpha)(\alpha\kappa-1)]}{(R/\alpha)(\alpha\kappa-1)}\right). \tag{9}$$

The electron energy $E = \kappa^2/2m$ is a function of R, and may be calculated by solving (9). The total energy of the H_2^+ ion is given by $E_T(R) = e^2/R - \kappa^2(R)/2m$, where the first term indicates the repulsion between protons. We find the occurrence of a minimum of energy at $R_0 = 0{\cdot}84$ Å, which is the equilibrium separation. This value is about 0·2 Å smaller than the experimental value (1·06 Å). The total energy of the system at R_0 is $E_T(R_0) = -15{\cdot}82$ eV, in good agreement to the experimental result $-16{\cdot}27$ eV [10]. The relative error is less than 3%. By analogy with the usual LCAO-MO techniques, these results may be improved, of course, by using a sum of NLP, each $v(\boldsymbol{r})$ function being a H-atom orbital times the Coulomb potential $1/r$. This realization could be used to describe excited states of the H_2^+ ion.

3. Crystal lattices

We consider a periodic arrangement of NLP to study the motion of electrons in period crystal lattices. We also take attractive potentials ($g > 0$) and consequently the Schrödinger equation for $E = -\kappa^2/2m < 0$ is written as

$$\begin{aligned}(\boldsymbol{p}^2+\kappa^2)\psi(\boldsymbol{r}) &= g\sum_{\boldsymbol{T}} v(|\boldsymbol{r}-\boldsymbol{T}|)\int \mathrm{d}^3r'\, v(|\boldsymbol{r}'-\boldsymbol{T}|)\psi(\boldsymbol{r}') \\ &= g\sum_{\boldsymbol{T}} v(|\boldsymbol{r}-\boldsymbol{T}|)\exp(\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{T})\int \mathrm{d}^3r'\, v(r')\psi(\boldsymbol{r}'),\end{aligned} \tag{10}$$

where $\boldsymbol{T}$ runs over lattice positions and we have used the Bloch theorem $\psi(\boldsymbol{r}+\boldsymbol{T}) = \exp(\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{T})\psi(\boldsymbol{r})$. Performing the Fourier transform of (10) and following the same steps as before we obtain

$$\frac{1}{4\pi g} = \sum_{\boldsymbol{T}} \exp(\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{T})\int_0^\infty \mathrm{d}p\,\frac{p^2|v(p)|^2}{p^2+\kappa^2}\frac{\sin(pT)}{pT}. \tag{11}$$

The coupling constant g may be expressed in terms of the bound state energy $E_0 = -\kappa_0^2/2m$ of the single-site potential. The energy E_0 is obtained by neglecting the effects of the lattice potential due to the other atoms. This may be carried out only considering the term corresponding to $\boldsymbol{T} = 0$ in the right hand side of (11). In so doing, we find

$$\frac{1}{4\pi g} = \int_0^\infty \mathrm{d}p\,\frac{p^2|v(p)|^2}{p^2+\kappa_0^2}. \tag{12}$$

Therefore, inserting (12) in (11) yields

$$\int_0^\infty \mathrm{d}p\,p^2|v(p)|^2\left(\frac{1}{p^2+\kappa_0^2}-\frac{1}{p^2+\kappa^2}\right) = \sum_{\boldsymbol{T}}{}' \exp(\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{T})\int_0^\infty \mathrm{d}p\,\frac{p^2|v(p)|^2}{p^2+\kappa^2}\frac{\sin(pT)}{pT}, \tag{13}$$

where the prime indicates the omission of the term $\boldsymbol{T} = 0$. We now cast the integrals

in the position space. Defining

$$I(\kappa) = \kappa \int_0^\infty dr \int_0^\infty dr'\, rv(r)r'v(r')(\exp(-\kappa|r - r'|) - \exp[-\kappa(r + r')]), \tag{14a}$$

$$J(\kappa) = \kappa \int_0^\infty dr\, rv(r) \sinh \kappa r, \tag{14b}$$

and the structural factor

$$F(\boldsymbol{K}, \kappa) = \sum_{\boldsymbol{T}}{}' \frac{1}{T} \exp[i(\boldsymbol{K} \cdot \boldsymbol{T} - \kappa T)], \tag{14c}$$

one finally gets

$$F(\boldsymbol{K}, \kappa) = [I(\kappa_0) - I(\kappa)]/2J^2(\kappa). \tag{15}$$

We observe that the structural factor only depends on the lattice geometry whereas the right-hand side depends on the exact form of the individual potentials. This enables us to separate the effects of the topological features of the lattice from those which manifest the pecularities of the single-site potential.

As an example we consider a linear chain of NLP of period L. This problem is of great interest to study linear polymer molecules, usually regarded as quasi-one-dimensional systems. In particular, polyacetylene $(CH)_x$ has been the focus of much of the experimental and theoretical work [11]. In this case, the structural factor (14c) may be calculated analytically. The result is

$$\frac{1}{L} \ln(2\cosh(\kappa L) - 2\cos(KL)) = \kappa + [I(\kappa_0) - I(\kappa)]/2J(\kappa). \tag{16}$$

The resulting band structure will depend on the shape function $v(r)$. One of the most simple functions is $v(r) = \delta(r - R)$, i.e. a force field vanishing everywhere except on a spherical shell of radius R. Using (14) and taking the limit $R \to 0$ in such a way that κ_0 remains constant, we find

$$\cos(KL) = \cosh(\kappa L) - \tfrac{1}{2}\exp(\kappa_0 L). \tag{17}$$

This expression has been formerly obtained by Demkov and Subramanian [1] within the SRP approximation, κ_0^{-1} being the scattering length of the single-site potential. We conclude that SRP results may be obtained as particular cases of our results. Real values of κ in (17), obtained by the usual search methods, give us the electron energy $E(K)$ and consequently the band structure of the lattice. At any value of $\kappa_0 L$, there exists one and only one band in the region of negative energies. For large values of κ_0 ($> \ln 4$) the band lies entirely in that energy region. The input parameters are L, which is usually known from X-ray data, and κ_0.

The effective mass of the particle may also be exactly calculated. This effective mass is

$$m^* = -m\left[\kappa\left(\frac{\partial^2 \kappa}{\partial K^2}\right)_{K=0}\right]^{-1}$$

and we obtain from the dispersion relation [1]

$$m^*/m = \frac{(\gamma^2 - 1)^{1/2}}{\ln[\gamma + (\gamma^2 - 1)^{1/2}]} \tag{18}$$

with $\gamma = \frac{1}{2}\exp(\kappa_0 L) + 1$. The remaining problem in the calculations of $E(K)$ and m^* is to evaluate κ_0. This can be done from the experimental band structure. Let E_t and E_b be the energy of the top and the bottom of the band, respectively ($KL = 0$ and $KL = \pi$), and let us define $\kappa_t^2 = -2mE_t$ and $\kappa_b^2 = -2mE_b$. From (17) we have

$$\kappa_0 L = \ln(\cosh(\kappa_t L) + \cosh(\kappa_b L)). \tag{19}$$

Now we apply these results to study the band structure of polyacetylene. Fink and Leising [11] have performed a tight binding calculation to obtain

$$E(K) = \pm[\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2\cos(KL)]^{1/2} \tag{20}$$

with $\beta_1 = 3{\cdot}64\,\text{eV}$ and $\beta_2 = 2{\cdot}75\,\text{eV}$. Their results are in good agreement with the observed band structure, although fail in explaining the effective mass. Using (20) we obtain $E_t = -0{\cdot}89\,\text{eV}$ and $E_b = -6{\cdot}39\,\text{eV}$. Taking $L = 1{\cdot}39\,\text{Å}$ for a uniform carbon–carbon bond length [12] we conclude that $\kappa_0 L = 1{\cdot}466$, corresponding to an energy level of the isolated potential of $-4{\cdot}23\,\text{eV}$. Inserting this value of $\kappa_0 L$ in (18) we get $m^*/m \simeq 1{\cdot}65$, in excellent agreement with the experimental result $m^*/m = 1{\cdot}7 \pm 0{\cdot}1$.

6. Conclusions

Nonlocal separable potentials may be used to obtain exactly solvable Schrödinger equations to be applied in several physical problems. Although there are no theoretical limitations to the precision of results, we have shown that even naive potentials lead to accurate results in a rather simple way.

References

[1] Demkov, Yu. N., and Subramanian, R., 1970, *Soviet Phys. JETP*, **30,** 381.
[2] Berezin, A. A., 1986, *Phys. Rev. B*, **33,** 2122.
[3] Bhagwat, K. V., and Subramanian, R., 1971, *Phys. Stat. Sol.* (*b*), **47,** 317.
[4] Newton, R. G., 1966, *Scattering Theory of Waves and Particles* (McGraw-Hill).
[5] Knight, B. W., and Peterson, G. A., 1963, *Phys. Rev.*, **132,** 1085.
[6] Sievert, P. R., and Glasser, M. L., 1973, *Phys. Rev. B*, **7,** 1265.
[7] Glasser, M. L., 1977, *Surf. Sci.*, **64,** 141.
[8] Bates, D. R., Ledshan, K., and Stewart, L., 1953, *Phil. Trans. R. Soc. London*, **246,** 215.
[9] Yamaguchi, Y., 1954, *Phys. Rev.*, **95,** 1628.
[10] Bransden, B. H., and Joachain, C. J., 1990, *Physics of Atoms and Molecules*, (Longman Scientific & Technical) p. 393.
[11] Fink, J., and Leising, G., 1986, *Phys. Rev. B*, **34,** 5320.
[12] Grant, P. M., and Batra, I. P., 1979, *Solid-St. Commun.*, **29,** 225.