

Justification of the Total Ionic Pseudopotentials in First-Principle Methods

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(Received September 24, 2009)

The total angular momentum basis used in the original semi-relativistic total ionic pseudopotential of the first-principle methods is transformed by the Clebsch-Gordan coefficients to the basis in which the orbital and spin angular momenta are not intermixed. With the transformed pseudopotential model, the procedures to obtain the non-relativistic total ionic pseudopotentials are justified as much as possible in this article. The justification process shows that the spin-orbit coupling effects can be included, at least partially, in a diagonal pseudopotential model that is formally close to the non-relativistic model.

PACS numbers: 71.10.-w, 71.15.Mb, 71.15.Rf

I. INTRODUCTION

In the first-principle calculations of molecules and solids [1], the effects of the core electrons of an atom are usually replaced by pseudopotentials [2], so that the valence electrons have energies, wavefunctions (beyond a certain cut-off radii), and scattering properties that are essentially unchanged from those of the full-core atom. The bare-ion potentials are obtained by subtracting the valence-electron potentials from the screened potentials. Frequently, the energies and wavefunctions of the full-core atoms are obtained relativistically by solving the Dirac equations [3, 4]. The total ionic pseudopotential to be used in different chemical environments is an operator expressed in terms of the total angular momentum states to account for the spin-orbital coupling nature of the Dirac equations. For the calculation of the chemical states of the valence electrons in a solid or a molecule, the Schrödinger equation is used [5, 6]. Hence, the relativistic total ionic pseudopotentials have to be recast in a form that can be used with the non-relativistic governing equation for valence electrons.

In modern *ab initio* packages [7–9], the bare-ion potentials associated with two different spin angular momenta states are frequently obtained relativistically. The two bare-ion potentials are averaged for non-relativistic first-principle calculations. The non-relativistic form of the total ionic pseudopotentials are widely used in many aspects of the pseudopotential theories [2, 10, 11].

In this article, the procedures for obtaining the non-relativistic pseudopotential from the relativistic model are justified as much as possible. Using a basis transformation, the approximations assumed for the reduction of the relativistic to non-relativistic models are revealed. Furthermore, by this justification process, it can be illustrated that the spin-orbit

coupling can be included, at least partially, in a pseudopotential formally similar to the non-relativistic model.

II. JUSTIFICATION

The total ionic pseudopotential to be used in different chemical environments is the operator expressed by [3]

$$\widehat{V}_{\text{ps}}^{\text{ion}}(r) = \sum_{\ell} \sum_{m'} \left[\left| \ell + \frac{1}{2}, m' \right\rangle V_{\ell, \ell + \frac{1}{2}}^{\text{ion}}(r) \left\langle \ell + \frac{1}{2}, m' \right| + \left| \ell - \frac{1}{2}, m' \right\rangle V_{\ell, \ell - \frac{1}{2}}^{\text{ion}}(r) \left\langle \ell - \frac{1}{2}, m' \right| \right], \quad (1)$$

where $V_{\ell, \ell \pm \frac{1}{2}}^{\text{ion}}(r)$ are the bare-ion potentials and $|\ell \pm \frac{1}{2}, m'\rangle$ are the total angular momentum states. This form is employed, for example, in relativistic fully separable pseudopotentials [12]. The index ℓ is the orbital angular momentum of the state $|\ell \pm \frac{1}{2}, m'\rangle \equiv |\ell, \frac{1}{2}; \ell \pm \frac{1}{2}, m'\rangle$ with the total angular momentum of $j = \ell \pm \frac{1}{2}$ and the magnetic quantum number of m' . Note that ℓ is an integer, whereas m' is a half-integer. The above pseudopotential is constructed with intrinsic spins, but the bare-ion potentials $V_{\ell, \ell \pm \frac{1}{2}}^{\text{ion}}(r)$ usually are not obtained entirely relativistically [4, 13, 14]. Hence, the total ionic pseudopotential is “semi-relativistic” in nature. Because the bare-ion potentials are real-valued, the semi-relativistic total ionic pseudopotential operators are Hermitian, $\widehat{V}_{\text{ps}}^{\text{ion}}(r)^\dagger = \widehat{V}_{\text{ps}}^{\text{ion}}(r)$. This Hermiticity of the total ionic pseudopotential operator is vitally important for its application.

The semi-relativistic total ionic pseudopotentials in Eq. (1) are expressed using the basis of $|\ell \pm \frac{1}{2}, m'\rangle$. By using the Clebsch-Gordan coefficients [15, 16], the semi-relativistic total ionic pseudopotentials can be transformed to a form in which the orbital angular momentum is separated from the spin. From the latter form, the non-relativistic total ionic pseudopotentials can be obtained when simplifying conditions are imposed.

Equation (1) can be rewritten in the matrix form

$$\widehat{V}_{\text{ps}}^{\text{ion}}(r) = \sum_{\ell} \sum_{m'} \left\{ \left[\left| \ell + \frac{1}{2}, m' \right\rangle, \left| \ell - \frac{1}{2}, m' \right\rangle \right] \mathbf{V} \begin{bmatrix} \left\langle \ell + \frac{1}{2}, m' \right| \\ \left\langle \ell - \frac{1}{2}, m' \right| \end{bmatrix} \right\} \quad (2)$$

with

$$\mathbf{V} = \begin{bmatrix} V_{\ell, \ell + \frac{1}{2}}^{\text{ion}}(r) & 0 \\ 0 & V_{\ell, \ell - \frac{1}{2}}^{\text{ion}}(r) \end{bmatrix}.$$

The Clebsch-Gordan coefficients relate the set of basis $|\ell \pm \frac{1}{2}, m'\rangle$ to another set by [15]

$$\begin{bmatrix} \left| \ell + \frac{1}{2}, m' \right\rangle \\ \left| \ell - \frac{1}{2}, m' \right\rangle \end{bmatrix} = \mathbf{B} \begin{bmatrix} \left| m' - \frac{1}{2}, \frac{1}{2} \right\rangle \\ \left| m' + \frac{1}{2}, -\frac{1}{2} \right\rangle \end{bmatrix} \quad (3)$$

with

$$\mathbf{B} = \frac{1}{\sqrt{2\ell+1}} \begin{bmatrix} \sqrt{\ell+m'+\frac{1}{2}} & \sqrt{\ell-m'+\frac{1}{2}} \\ -\sqrt{\ell-m'+\frac{1}{2}} & \sqrt{\ell+m'+\frac{1}{2}} \end{bmatrix},$$

where $|m' \mp \frac{1}{2}, \pm \frac{1}{2}\rangle \equiv |\ell, \frac{1}{2}; m' \mp \frac{1}{2}, \pm \frac{1}{2}\rangle = |\ell, m' \mp \frac{1}{2}\rangle \otimes |\frac{1}{2}, \pm \frac{1}{2}\rangle$ is the basis set where the orbital and spin angular momenta are separated. The operator \otimes stands for the direct product between the orbital and spin angular momenta. From Eq. (3), the following two matrix relations can be obtained:

$$[|\ell + \frac{1}{2}, m'\rangle, |\ell - \frac{1}{2}, m'\rangle] = [|m' - \frac{1}{2}, \frac{1}{2}\rangle, |m' + \frac{1}{2}, -\frac{1}{2}\rangle] \mathbf{B}^T$$

and

$$\begin{bmatrix} \langle \ell + \frac{1}{2}, m' | \\ \langle \ell - \frac{1}{2}, m' | \end{bmatrix} = \mathbf{B} \begin{bmatrix} \langle m' - \frac{1}{2}, \frac{1}{2} | \\ \langle m' + \frac{1}{2}, -\frac{1}{2} | \end{bmatrix}.$$

Substituting the above two equations into Eq. (2), the semi-relativistic total ionic pseudopotential becomes

$$\widehat{V}_{\text{ps}}^{\text{ion}}(r) = \sum_{\ell} \sum_{m'} \left\{ [|m' - \frac{1}{2}, \frac{1}{2}\rangle, |m' + \frac{1}{2}, -\frac{1}{2}\rangle] \mathbf{V}' \begin{bmatrix} \langle m' - \frac{1}{2}, \frac{1}{2} | \\ \langle m' + \frac{1}{2}, -\frac{1}{2} | \end{bmatrix} \right\},$$

where

$$\mathbf{V}' = \mathbf{B}^T \mathbf{V} \mathbf{B} = \frac{1}{2\ell+1} \begin{bmatrix} (\ell+m'+\frac{1}{2})V_{\ell, \ell+\frac{1}{2}}^{\text{ion}}(r) & \sqrt{(\ell+m'+\frac{1}{2})(\ell-m'+\frac{1}{2})} \\ +(\ell-m'+\frac{1}{2})V_{\ell, \ell-\frac{1}{2}}^{\text{ion}}(r) & \times [V_{\ell, \ell+\frac{1}{2}}^{\text{ion}}(r) - V_{\ell, \ell-\frac{1}{2}}^{\text{ion}}(r)] \\ \sqrt{(\ell+m'+\frac{1}{2})(\ell-m'+\frac{1}{2})} & (\ell-m'+\frac{1}{2})V_{\ell, \ell+\frac{1}{2}}^{\text{ion}}(r) \\ \times [V_{\ell, \ell+\frac{1}{2}}^{\text{ion}}(r) - V_{\ell, \ell-\frac{1}{2}}^{\text{ion}}(r)] & +(\ell+m'+\frac{1}{2})V_{\ell, \ell-\frac{1}{2}}^{\text{ion}}(r) \end{bmatrix}.$$

The matrix \mathbf{V}' is real-valued and symmetric. Changing the indices by $m = m' - \frac{1}{2}$, the total ionic pseudopotential is further written as

$$\widehat{V}_{\text{ps}}^{\text{ion}}(r) = \sum_{\ell} \sum_m \left\{ [|[\frac{1}{2}, \frac{1}{2}] \otimes |\ell, m\rangle, |\frac{1}{2}, -\frac{1}{2}] \otimes |\ell, m+1\rangle] \mathbf{V}' \begin{bmatrix} \langle \ell, m | \otimes \langle \frac{1}{2}, \frac{1}{2} | \\ \langle \ell, m+1 | \otimes \langle \frac{1}{2}, -\frac{1}{2} | \end{bmatrix} \right\} \quad (4)$$

with

$$\mathbf{V}' = \frac{1}{2\ell+1} \begin{bmatrix} (\ell+m+1)V_{\ell, \ell+\frac{1}{2}}^{\text{ion}}(r) & \sqrt{(\ell+m+1)(\ell-m)} \\ +(\ell-m)V_{\ell, \ell-\frac{1}{2}}^{\text{ion}}(r) & \times [V_{\ell, \ell+\frac{1}{2}}^{\text{ion}}(r) - V_{\ell, \ell-\frac{1}{2}}^{\text{ion}}(r)] \\ \sqrt{(\ell+m+1)(\ell-m)} & (\ell-m)V_{\ell, \ell+\frac{1}{2}}^{\text{ion}}(r) \\ \times [V_{\ell, \ell+\frac{1}{2}}^{\text{ion}}(r) - V_{\ell, \ell-\frac{1}{2}}^{\text{ion}}(r)] & +(\ell+m+1)V_{\ell, \ell-\frac{1}{2}}^{\text{ion}}(r) \end{bmatrix}, \quad (5)$$

where, unlike m' , the index m is an integer, and the angular momentum states are explicitly written as the direct product of orbital angular momentum and spin. The orbital angular momentum and spin are no longer intermixed. As expected, the Hermiticity of the operator $\widehat{V}_{\text{ps}}^{\text{ion}}(r)$ is retained in the form given by Eq. (4).

Using the 2×2 matrix representation of the spin space, the semi-relativistic total ionic pseudopotential with the elements $\langle \frac{1}{2}, m_s | \widehat{V}_{\text{ps}}^{\text{ion}}(r) | \frac{1}{2}, m'_s \rangle$, m_s , and $m'_s = \pm \frac{1}{2}$ becomes

$$\widehat{V}_{\text{ps}}^{\text{ion}}(r) = \sum_{\ell} \sum_m \frac{1}{2\ell+1} \begin{bmatrix} |\ell, m\rangle \left[(\ell+m+1)V_{\ell, \ell+\frac{1}{2}}^{\text{ion}}(r) & |\ell, m\rangle \sqrt{(\ell+m+1)(\ell-m)} \right. \\ \left. + (\ell-m)V_{\ell, \ell-\frac{1}{2}}^{\text{ion}}(r) \right] \langle \ell, m| & \times \left[V_{\ell, \ell+\frac{1}{2}}^{\text{ion}}(r) - V_{\ell, \ell-\frac{1}{2}}^{\text{ion}}(r) \right] \langle \ell, m+1| \\ |\ell, m+1\rangle \sqrt{(\ell+m+1)(\ell-m)} & |\ell, m\rangle \left[(\ell-m+1)V_{\ell, \ell+\frac{1}{2}}^{\text{ion}}(r) \right. \\ \left. \times \left[V_{\ell, \ell+\frac{1}{2}}^{\text{ion}}(r) - V_{\ell, \ell-\frac{1}{2}}^{\text{ion}}(r) \right] \langle \ell, m| & \left. + (\ell+m)V_{\ell, \ell-\frac{1}{2}}^{\text{ion}}(r) \right] \langle \ell, m| \end{bmatrix}, \quad (6)$$

where the index has been changed in the matrix element $\langle \frac{1}{2}, -\frac{1}{2} | \widehat{V}_{\text{ps}}^{\text{ion}}(r) | \frac{1}{2}, -\frac{1}{2} \rangle$ by shifting from $m+1$ to m . Not surprisingly, $\widehat{V}_{\text{ps}}^{\text{ion}}(r)$ is a 2×2 Hermitian matrix of operators:

$$\left[\widehat{V}_{\text{ps}}^{\text{ion}}(r) \right]^{\dagger} = \widehat{V}_{\text{ps}}^{\text{ion}}(r).$$

Using the notation $|\vec{r}, m_s\rangle = |\vec{r}\rangle \otimes |\frac{1}{2}, m_s\rangle = |r, \theta, \phi\rangle \otimes |\frac{1}{2}, m_s\rangle$ with $m_s = \pm \frac{1}{2}$, the semi-relativistic total ionic pseudopotential in real space, $\langle \vec{r}' | \widehat{V}_{\text{ps}}^{\text{ion}}(r) | \vec{r}' \rangle$, reads

$$\mathbf{V}_{\text{ps}}^{\text{ion}}(\vec{r}, \vec{r}') = \frac{1}{4\pi} \delta(r-r') \sum_{\ell} (2\ell+1) \begin{bmatrix} P_{\ell}(\xi) \bar{V}_{\ell}^{\text{ion}}(r) & (e^{-i\phi} \cos \theta' \sin \theta \\ -i \sin \theta \sin \theta' \sin(\phi' - \phi) & -e^{-i\phi'} \cos \theta \sin \theta' \\ \times P'_{\ell}(\xi) \cdot \frac{1}{2} V_{\ell}^{\text{so}}(r) & \times P'_{\ell}(\xi) \cdot \frac{1}{2} V_{\ell}^{\text{so}}(r) \\ \\ (e^{i\phi'} \cos \theta \sin \theta' & P_{\ell}(\xi) \bar{V}_{\ell}^{\text{ion}}(r) \\ -e^{i\phi} \cos \theta' \sin \theta & +i \sin \theta \sin \theta' \sin(\phi' - \phi) \\ \times P'_{\ell}(\xi) \cdot \frac{1}{2} V_{\ell}^{\text{so}}(r) & \times P'_{\ell}(\xi) \cdot \frac{1}{2} V_{\ell}^{\text{so}}(r) \end{bmatrix}, \quad (7)$$

where $P_{\ell}(\xi)$ is the Legendre polynomial of order ℓ and $P'_{\ell}(\xi)$ is its first derivative. The inner product of the unit vectors $\hat{r} = \frac{\vec{r}}{r}$ and $\hat{r}' = \frac{\vec{r}'}{r'}$ is denoted by $\xi = \hat{r} \cdot \hat{r}' = \sin \theta \cos \phi \sin \theta' \cos \phi' + \sin \theta \sin \phi \sin \theta' \sin \phi' + \cos \theta \cos \theta'$, where θ and ϕ are the azimuth and polar angles of the unit vector \hat{r} , respectively; similarly for \hat{r}' . The summations over m have been performed in the above equation. Note that $\mathbf{V}_{\text{ps}}^{\text{ion}}(\vec{r}, \vec{r}')$ in Eq. (7) is a 2×2 matrix of complex numbers. Because $\langle \vec{r}' | \widehat{V}_{\text{ps}}^{\text{ion}}(r) | \vec{r}' \rangle^* = \langle \vec{r}' | \widehat{V}_{\text{ps}}^{\text{ion}}(r) | \vec{r} \rangle$, the Hermiticity of the semi-relativistic total ionic pseudopotential in real space takes the form of

$$\left[\mathbf{V}_{\text{ps}}^{\text{ion}}(\vec{r}, \vec{r}') \right]^{\dagger} \Big|_{\vec{r}' \leftrightarrow \vec{r}} = \mathbf{V}_{\text{ps}}^{\text{ion}}(\vec{r}, \vec{r}'),$$

where, in addition to complex-conjugating the matrix elements and interchanging rows and columns, the space variables have to be exchanged on the left-hand side of the relation.

The real-space matrix elements of the total ionic pseudopotential $\mathbf{V}_{\text{ps}}^{\text{ion}}(\vec{r}, \vec{r}')$ in Eq. (7) are complex-valued. This is due to the fact that the total ionic pseudopotential operator $\widehat{V}_{\text{ps}}^{\text{ion}}(r)$ in Eq. (1) is semi-relativistic. If the above semi-relativistic ionic pseudopotential is to be used with the Schrödinger equation, the intrinsic spin has to be artificially separated.

In practice, the bare-ion pseudopotentials $V_{\ell, \ell \pm \frac{1}{2}}^{\text{ion}}(r)$ in the total ionic pseudopotential $\widehat{V}_{\text{ps}}^{\text{ion}}(r)$ of Eq. (1) are obtained by matching the Schrödinger solutions to the self-consistent Dirac solutions of the valence electrons. Therefore, it is not meaningful to use these pseudopotentials with governing equations more accurate than the Schrödinger equation, such as the Dirac or Dirac-like equations [17]. The total ionic pseudopotentials in Eq. (1) are created with spins, but spins are not intrinsic to the Schrödinger equation. Therefore, the semi-relativistic total ionic pseudopotential operator $\widehat{V}_{\text{ps}}^{\text{ion}}(r)$ has to be modified if it is to be used with the Schrödinger equation. The intrinsic spin-dependence can be separated under the simplifying conditions given below.

If the off-diagonal elements of the matrix \mathbf{V}' in Eq. (5) are ignored, the matrix \mathbf{V}' becomes diagonal. As a result, the total ionic pseudopotential in Eq. (4) becomes the diagonal model of

$$\begin{aligned} \widehat{V}_{\text{ps,D}}^{\text{ion}}(r) = \sum_{\ell} \sum_m \left\{ \left| \frac{1}{2}, \frac{1}{2} \right\rangle \otimes |\ell, m\rangle \left[\overline{V}_{\ell}^{\text{ion}}(r) + \frac{m}{2} V_{\ell}^{\text{so}}(r) \right] \langle \ell, m | \otimes \left\langle \frac{1}{2}, \frac{1}{2} \right| \right. \\ \left. + \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \otimes |\ell, m\rangle \left[\overline{V}_{\ell}^{\text{ion}}(r) - \frac{m}{2} V_{\ell}^{\text{so}}(r) \right] \langle \ell, m | \otimes \left\langle \frac{1}{2}, -\frac{1}{2} \right| \right\} \quad (8) \end{aligned}$$

with

$$\overline{V}_{\ell}^{\text{ion}}(r) = \frac{1}{2\ell + 1} \left[(\ell + 1) V_{\ell, \ell + \frac{1}{2}}^{\text{ion}}(r) + \ell V_{\ell, \ell - \frac{1}{2}}^{\text{ion}}(r) \right] \quad (9)$$

and

$$V_{\ell}^{\text{so}}(r) = \frac{2}{2\ell + 1} \left[V_{\ell, \ell + \frac{1}{2}}^{\text{ion}}(r) - V_{\ell, \ell - \frac{1}{2}}^{\text{ion}}(r) \right], \quad (10)$$

where the index of the term previously involving $|\ell, m + 1\rangle$ has been changed by shifting from $m + 1$ to m . This shifting of indices is possible only if the matrix \mathbf{V}' is diagonal. $\overline{V}_{\ell}^{\text{ion}}(r)$ in Eq. (9) is the pseudopotential averaged with the weights of the m' -degeneracies; whereas $V_{\ell}^{\text{so}}(r)$ in Eq. (10) is the term corresponding to the spin-orbit coupling effects. Note that the diagonal elements of \mathbf{V}' expressed as

$$\overline{V}_{\ell}^{\text{ion}}(r) \pm \frac{m}{2} V_{\ell}^{\text{so}}(r) = \frac{1}{2\ell + 1} \left[(\ell \pm m + 1) V_{\ell, \ell + \frac{1}{2}}^{\text{ion}}(r) + (\ell \mp m) V_{\ell, \ell - \frac{1}{2}}^{\text{ion}}(r) \right] \quad (11)$$

are used. Using the total ionic pseudopotentials in Eq. (8) is termed the diagonal model in this work because of the diagonal approximation.

If the spin-orbit coupling terms in the diagonal elements are ignored as well, then all spin-orbit coupling effects are neglected. The ionic pseudopotential becomes the non-spin-

orbit (NSO) coupling model,

$$\begin{aligned} \widehat{V}_{\text{ps,NSO}}^{\text{ion}}(r) &= \sum_{\ell} \sum_m \\ &\left\{ \left| \frac{1}{2}, \frac{1}{2} \right\rangle \otimes |\ell, m\rangle \overline{V}_{\ell}^{\text{ion}}(r) \langle \ell, m| \otimes \left\langle \frac{1}{2}, \frac{1}{2} \right| + \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \otimes |\ell, m\rangle \overline{V}_{\ell}^{\text{ion}}(r) \langle \ell, m| \otimes \left\langle \frac{1}{2}, -\frac{1}{2} \right| \right\} \\ &= \widehat{P}_s \left[\sum_{\ell} \sum_m |\ell, m\rangle \overline{V}_{\ell}^{\text{ion}}(r) \langle \ell, m| \right] \widehat{P}_s, \end{aligned} \quad (12)$$

with the projection operator in the spin space being given by $\widehat{P}_s = \left| \frac{1}{2}, \frac{1}{2} \right\rangle \left\langle \frac{1}{2}, \frac{1}{2} \right| + \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \left\langle \frac{1}{2}, -\frac{1}{2} \right|$. For spinless computations, the projection operator \widehat{P}_s in the above equation can be removed, and the non-relativistic total ionic pseudopotential reads [18]

$$\widehat{V}_{\text{ps,NR}}^{\text{ion}}(r) = \sum_{\ell} \sum_m |\ell, m\rangle \overline{V}_{\ell}^{\text{ion}}(r) \langle \ell, m|, \quad (13)$$

where $|\ell, m\rangle$ is the state with the orbital angular momentum ℓ and the magnetic quantum number m . Both ℓ and m are integers. The above non-relativistic total ionic pseudopotential involves the average of bare-ion potentials associated with angular momenta $\ell + \frac{1}{2}$ and $\ell - \frac{1}{2}$.

From the above justification process, it can be seen that two approximation steps are involved in proceeding from the semi-relativistic total ionic pseudopotential in Eq. (1) to the non-relativistic one in Eq. (13). First, the off-diagonal elements in the matrix of Eqs. (4) and (5) resulting from the basis transformation are ignored. In this first approximation step, the semi-relativistic pseudopotential is reduced to the diagonal pseudopotential in Eq. (8). Second, the spin-orbit coupling terms involving $V_{\ell}^{\text{so}}(r)$ in the diagonal pseudopotential are further neglected. After the second approximation step, the diagonal pseudopotential is simplified to be the non-relativistic pseudopotential in Eq. (13).

If the two-step approximation ceases after the first step, the diagonal pseudopotential emerges. The diagonal pseudopotential $\widehat{V}_{\text{ps,D}}^{\text{ion}}(r)$ in Eq. (8) formally resembles the NSO pseudopotential $\widehat{V}_{\text{ps,NSO}}^{\text{ion}}(r)$ in Eq. (12). In contrast to the NSO model, the diagonal pseudopotential model retains, at least in part, the spin-orbit interactions because of the presence of the term $\frac{m}{2} V_{\ell}^{\text{so}}(r)$ in the diagonal elements of the matrix.

III. CONCLUSION

The semi-relativistic total ionic pseudopotentials for first-principle methods are expressed in the literature with the basis set of the total angular momenta. The basis set is transformed by the Clebsch-Gordan coefficients to another set in which the orbital and spin angular momenta are separated. It is demonstrated that the negligence of the off-diagonal elements of the transformation matrix results in the diagonal pseudopotential, and that further negligence of the spin-orbit terms in the diagonal model leads to the non-relativistic model of the total ionic pseudopotential. The justification process not only illustrates the

approximation steps involved in reducing the semi-relativistic to non-relativistic pseudopotentials but also shows that the spin-orbit coupling can be included, at least partially, in the diagonal pseudopotential that is formally close to the non-relativistic pseudopotential model.

Acknowledgements

T. L. Li and W. S. Su would like to acknowledge the support of the National Science Council of Taiwan by Grant Nos. NSC-99-2112-M-415-008 and NSC-99-2112-M-492-001-MY2, respectively. They would also like to acknowledge the support of the National Center for Theoretical Sciences and the National Center for High-Performance Computing of Taiwan.

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