

On the Wigner–Witmer correlation rules for a homonuclear diatomic molecule with the like atoms in identical atomic states

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Abstract. The problem of building the manifold of electronic states of a homonuclear diatomic molecule formed from two like atoms in identical atomic states is readdressed. A conceptually simple approach is presented by invoking a model and all the standard results originally obtained by Wigner and Witmer are reproduced.

Keywords. Homonuclear molecules; Wigner–Witmer rules; diatomic states.

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1. Introduction

The rules for building the electronic states of a diatomic molecule from those of the constituent atoms were expounded by Wigner and Witmer in a masterly paper [1] well over half a century ago. These ‘Wigner–Witmer correlation rules’ have been subsequently discussed by Herzberg [2], Landau and Lifshitz [3] and Chiu [4] from the standpoints of the vector atom model, molecular quantum mechanics and projection operators. A majority of these rules seem intuitively plausible and their validity is easily demonstrated [3]. One notable exception is the rule for correlating states in the manifold of electronic states of a homonuclear diatomic molecule built from two like atoms in *identical* atomic states. We recall that for a homonuclear molecule, the *gerade* (*g*) or *ungerade* (*u*) parity of its electronic state becomes an important attribute. When the molecule is built from two identical atoms, each in the same electronic state, the *g* or *u* character of the resulting molecular state, its Λ (component of net electronic orbital angular momentum along the figure axis) and spin multiplicity are inter-linked and the answer to the question of how one may tag the *u*, *g* label onto the molecular state with definite Λ and spin multiplicity is not all that obvious. To put things in a better perspective, we present a few typical results in table 1 which is a partial reproduction of a more exhaustive table contained in [2]. Referring to table 1, it is not quite obvious why, for instance, a $^4S + ^4S$ atomic state combination (as would happen when two nitrogen atoms in the normal state are brought together to form the N_2 molecule) should give rise precisely to $^1\Sigma_g^+$, $^3\Sigma_u^+$, $^5\Sigma_g^+$, $^7\Sigma_u^+$, but not to the set of states with the *u*, *g* labels swapped between them. The original work of

Table 1. Correlation of the electronic states of a homonuclear diatomic molecule resulting from the separated like atoms in identical atomic states.

| States of the separated atoms | Molecular states |
|-------------------------------|---|
| $^1S+^1S$ | $^1\Sigma_g^+$ |
| $^2S+^2S$ | $^1\Sigma_g^+, ^3\Sigma_u^+$ |
| $^3S+^3S$ | $^1\Sigma_g^+, ^3\Sigma_u^+, ^5\Sigma_g^+$ |
| $^4S+^4S$ | $^1\Sigma_g^+, ^3\Sigma_u^+, ^5\Sigma_g^+, ^7\Sigma_u^+$ |
| $^1P+^1P$ | $^1\Sigma_g^+(2), ^1\Sigma_u^-, ^1\Pi_g, ^1\Pi_u, ^1\Delta_g$ |
| $^2P+^2P$ | $^1\Sigma_g^+(2), ^1\Sigma_u^-, ^1\Pi_g, ^1\Pi_u, ^1\Delta_g, ^3\Sigma_u^+(2),$ $^3\Sigma_g^-, ^3\Pi_g, ^3\Pi_u, ^3\Delta_u$ |

Wigner and Witmer settles such questions by arguments based on the properties of permutation groups as applied to a complex many electron system consisting of the two atoms. To the practising molecular spectroscopist, the importance of the results like those contained in table 1 cannot be overemphasised. But despite the fact that abundant use has been made of these rules over the years for elucidating the dissociation products of electronic states of homonuclear diatomic molecules [2], the original paper of Wigner and Witmer [1] remains the only source to turn to for a rigorous derivation of the results. We emphasise that even the celebrated treatise by Landau and Lifshitz (which, otherwise, is a veritable repository of many such subtle demonstrations) has omitted the proof of this important set of rules on 'account of its length' [3]. The only available source material namely, the paper of Wigner and Witmer [1], apart from leaning heavily on group theoretical methods, is written in the German language and uses archaic terminology thus making its contents inaccessible to the English speaking readers. Inevitably therefore, a formal proof of these rather elegant correlation rules has remained elusive to a majority of the serious researchers in diatomic spectroscopy. This situation set us on a quest for an alternative, less taxing, demonstration of the Wigner–Witmer rules contained in table 1. In this process we have come up with a novel approach based on a model [5] that affords a conceptual simplification of the problem. The details of this method form the theme of the present paper. The derivation to be presented below is easy to comprehend. Since no prior knowledge of permutation groups is assumed, the approach may be included in a classroom lecture course.

2. Description of the model and theoretical details

The model that we wish to describe is essentially suggested by the Heitler–London (H–L) treatment of the H_2 molecule [2]. But unlike in the H_2 problem where the H–L method primarily treats the energies of the electronic states, our objective here is limited to formally constructing the molecular state from the states of the two like atoms in identical atomic states, and examining its symmetry in relation to its spin multiplicity. Consider the formation of the homonuclear molecule X_2 from the atomic combination $X + X$ with each X in the same atomic state $|nLM, S\sigma\rangle$. Here M and σ are, respectively, the 'z-component'

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(along the molecular axis) of the net orbital and spin angular momenta L and S . As a purely conceptual artifact, we replace each real atom X by a fictitious atom X^c consisting of a single particle moving in a spherically symmetric attractive potential centred at the corresponding nucleus. To this particle, which we shall sometimes refer to as the ‘quasi-electron’, we now ascribe an orbital angular momentum labelled by the quantum number L and intrinsic spin S so that the state of X^c too, may be represented as $|nLM, S\sigma\rangle$. Note that a potential with spherical symmetry is needed to characterise the model atom X^c by a well-defined orbital angular momentum. Thus the fictitious particle so introduced is made to play the collective role of all the electrons put together. The mass of the particle, its charge and the nature of the central potential (as long as it is sufficiently attractive to allow bound states) are attributes which are irrelevant to the problem on hand. The states of the real atom X and conceptual atom X^c are now in correspondence and we expect a similar correspondence to hold between the manifold of molecular states of X_2 and of X_2^c .

A few theoretical points are now in order. For the one particle atom X^c , we may write the orbital wave function as

$$\Psi_{nLM}^{\text{orb}}(\mathbf{r}) = R_{nL}(r)Y_{LM}(\theta, \varphi) \quad (1)$$

where $Y_{LM}(\theta, \varphi)$ is a spherical harmonic and $R_{nL}(r)$ is the radial part. When the two atoms $X^c + X^c$ are brought together to form the molecule X_2^c as shown in figure 1, we may use the H–L approach [2, 6] to form the molecular ‘electronic’ states as suitable linear combinations of products of the atomic states. Restricting ourselves to the orbital part,

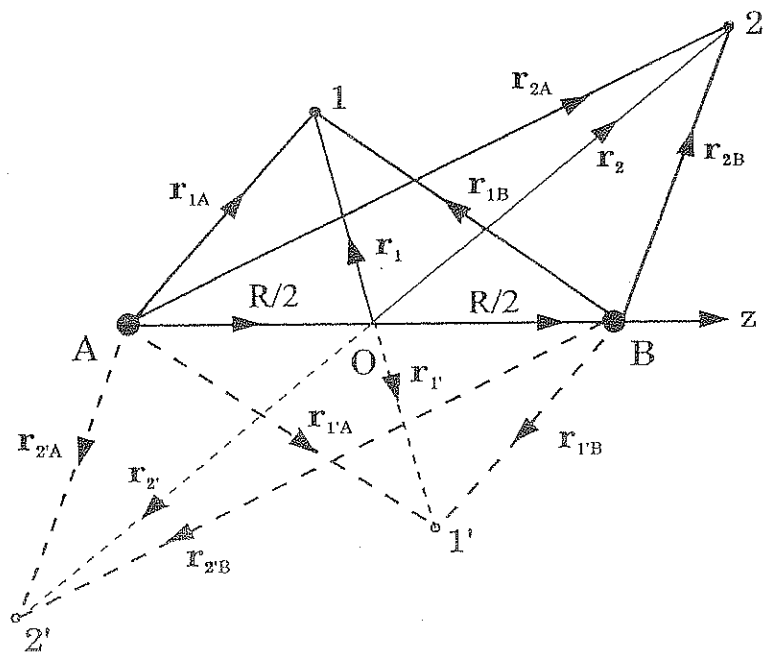


Figure 1. Effect of inversion \hat{I} at the geometric centre O on the positional coordinates of the quasi-electrons 1 and 2, both in relation to O as well as to the fixed ‘nuclei’ A and B .

two types of molecular states may be formed taking into account the 'exchange degeneracy', one that is symmetric under permutation of the particles 1 and 2 and the second, antisymmetric under such an exchange. The explicit manner in which such wave functions are to be constructed will be explained later. The total wave function of the molecule X_2^c should, of course, include the resultant spin of the two quasi-electrons as well. We may thus write

$$\Psi_{\text{Tot}}(1, 2) = \Psi_{\text{orb}}(1, 2) \cdot \chi_s(1, 2; S_m \Sigma) \quad (2)$$

where χ_s is the spin part, S_m is the spin of the molecular state and Σ is the related spin 'projection' quantum number. We now stipulate that $\Psi_{\text{Tot}}(1, 2)$ display the correct symmetry upon interchange of the identical particles 1 and 2. Since in our model we have ascribed an intrinsic spin S (= the net electronic spin in the given state of the original atom) to each of the particles 1 and 2, we must require that

$$\Psi_{\text{Tot}}(2, 1) = \begin{cases} +\Psi_{\text{Tot}}(1, 2) & \text{for integral } S \\ -\Psi_{\text{Tot}}(1, 2) & \text{for half-integral } S. \end{cases} \quad (3)$$

It is useful to recognize that the validity of the requirement implied by equation (3) goes beyond the states of the model diatom X_2^c and applies equally to the corresponding states of the real molecule X_2 . In the latter case the exchanging of the virtual single particles 1 and 2 would be tantamount to exchanging two equivalent groups of electrons (say, the valence electrons) between the two real atoms. If the total spin in the atomic state is integral (half integral), the number of electrons so exchanged would be even (odd) and therefore, the total wave function of the state of the real system X_2 will have to be symmetric (antisymmetric) in conformity with the requirement of eq. (3). This feature is also suggestive of the hidden connection between the present approach and the original derivation of Wigner and Witmer [1].

Let us first discuss the symmetry properties of the spin part χ_s in (2), being much easier. The $2S_m + 1$ spin functions $\chi_s(1, 2; S_m \Sigma)$, with $\Sigma = -S_m, -S_m + 1, \dots, +S_m$ for any given value of S_m are diagonal in $S_m^2 = (S_1 + S_2)^2$ and $S_{mz} = (S_{1z} + S_{2z})$. They are easy to construct from the product states $\{|1; S\sigma\rangle\} \otimes \{|2; S\sigma'\rangle\}$ as appropriate linear combinations and inherently display definite symmetry under the interchange of 1 and 2. The possible values S_m can assume are: $2S (= S + S)$, $2S - 1 (= S + S - 1)$, \dots , $0 (= S - S)$. It turns out that the spin states $\chi_s(1, 2; S_m \Sigma)$ for $S_m = 2S, 2S - 2, 2S - 4, \dots$ are symmetric while those for $S_m = 2S - 1, 2S - 3, \dots$ are antisymmetric, upon interchange of 1 and 2. (This simple property of the resultant spin states of a composite system with two identical parts each with the same inner angular momentum, has been discussed by Herzberg [2] in the context of the nuclear statistical weights of rotational levels in a homonuclear diatomic molecule).

Turning now to the orbital part, it will be shown later that the g or u character of $\Psi_{\text{orb}}(1, 2)$ that is, its behaviour under inversion \hat{I} of the coordinates of particles 1 and 2 at the geometric centre of the two nuclei, is intimately connected with its symmetry under the permutation of the particles 1 and 2. This coupled with the property of the resultant spin states on the one hand and requirement of eq. (3) on the other, severely restricts the manner in which the g, u labels of the molecular state with definite Λ may be correlated to its spin multiplicity.

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Before we apply these ideas to derive some typical results stated in table 1, it is necessary to construct the H–L type molecular wave function Ψ_{orb} from the orbital part of the atomic wave function in a general case. For this purpose we refer to figure 1. At infinite ‘bond’ distance, particle 1 and ‘nucleus’ A constitute one of the atoms while particle 2 and ‘nucleus’ B make up the other. Henceforth we shall take the internuclear axis AB as the z-axis and use it for quantization of L or S . Similar to the H–L procedure for obtaining the wave function for the H_2 molecule, the unnormalized molecular wave function for X_2^{\pm} with well-defined net orbital angular momentum projection Λ along the z-axis may be written down as

$$\Psi_{\text{orb}}(1, 2, \Lambda, \pm, p) = [\psi_{nLM}(\mathbf{r}_{1A})\psi_{nLM'}(\mathbf{r}_{2B}) \pm \psi_{nLM'}(\mathbf{r}_{1A})\psi_{nLM}(\mathbf{r}_{2B})] \\ + p[\psi_{nLM}(\mathbf{r}_{2A})\psi_{nLM'}(\mathbf{r}_{1B}) \pm \psi_{nLM'}(\mathbf{r}_{2A})\psi_{nLM}(\mathbf{r}_{1B})]. \quad (4)$$

Here $\Lambda = |M + M'|$ and p serves as an exchange symmetry label which can take the value +1 or –1. States with $p = +1$ are symmetric upon interchange of 1 and 2 and we denote such states as $\psi_{\text{orb}}(1, 2, \Lambda, \pm, s)$. The other choice $p = -1$ gives rise to antisymmetric orbital states $\Psi_{\text{orb}}(1, 2, \Lambda, \pm, a)$. It is useful to note a few points about these H–L functions. First, the interchange of M and M' leads essentially to the same set of functions. Next, for $M = M'$, the state $\Psi_{\text{orb}}(1, 2, \Lambda, -, p)$, vanishes identically irrespective of the choice of p and such a state cannot occur. Thirdly, in the present convention $\Lambda \geq 0$ and the state with given M, M' and $\Lambda \neq 0$, and the one obtained by reversing simultaneously the signs of M, M' , form degenerate Λ -doublets.

At this stage, it is appropriate to make a few remarks about the Σ states ($\Lambda = 0$) that can arise in the context of eq. (4). For Σ states it is important to distinguish between Σ^+ and Σ^- . This property depends on the behaviour of the orbital function under reflection σ_v in a plane passing through the intermolecular axis [2]. For $M = M' = 0$, only the + sign in eq. (4) holds and the resulting state is Σ^+ , since in that case none of the functions appearing on the right hand side of eq. (4) taken together with eq. (1), has any dependence on the azimuthal angles φ_1, φ_2 which alone are affected by the planar reflection operation. When $M' = -M \neq 0$, eq. (4) allows both + and – signs in the orbital function $\Psi(1, 2, \Lambda; \pm, p)$. The former leads to a Σ^+ state and the latter to Σ^- . This result follows readily from the fact that under σ_v , each product function transforms as

$$\sigma_v \psi_{nLM}(\mathbf{r}_{1A})\psi_{nL-M'}(\mathbf{r}_{2B}) = (-)^M (-)^{-M'} \psi_{nL-M}(\mathbf{r}_{1A})\psi_{nLM}(\mathbf{r}_{2B}) \text{ etc.}$$

In the last step we have used the fact $Y_{LM}(\theta, -\varphi) = (-)^M Y_{L-M}(\theta, \varphi)$. It remains to examine the g or u character of the states constructed in accordance with eq. (4). For this it is necessary to investigate the behaviour of the above functions under the operation \hat{i} which inverts the coordinates of the quasi-electrons 1 and 2 at the geometric centre of A and B (figure 1). It turns out that the functions $\Psi_{\text{orb}}(1, 2, \Lambda, +, s)$ and $\Psi_{\text{orb}}(1, 2, \Lambda, -, a)$ are left unaffected by \hat{i} and thus constitute ‘ g ’ states, while $\Psi_{\text{orb}}(1, 2, \Lambda, -, s)$ and $\Psi_{\text{orb}}(1, 2, \Lambda, +, a)$ change sign upon inversion and must thus carry the ‘ u ’ label. The proof of this statement is relegated to the appendix. The final step is to combine the orbital function with the appropriate spin function so that $\Psi_{\text{Tot}}(1, 2)$ displays the correct symmetry as required by eq. (3).

Following this procedure, all the results listed in the original table in ref. [2] may be derived. By way of illustration, the diatomic states arising from the four like-atom

Table 2. Symmetry of Heitler-London type orbital and spin functions of the homonuclear molecule X_2^c built from two conceptual atoms (X^c), each in the same atomic state.

| Atomic state combination | M | M' | $\psi_{\text{orb}}(1, 2)$ | | g/u | $\chi_{\text{spin}}(1, 2)$ | | $\Psi_{\text{Tot}}(1, 2)$ | Resulting states | |
|--------------------------|-------------|---------|---------------------------|-----------------------------|------------------------|----------------------------|-------|---------------------------|------------------------------|--------------|
| | | | Λ | $ \Lambda, \pm, s/a\rangle$ | | S_m | s/a | | | |
| $^3S + ^3S$ | 0 | 0 | 0 | $ \Sigma, +, s\rangle$ | g | 2, 0 | s | s | $^5\Sigma_g^+, ^1\Sigma_g^+$ | |
| | 0 | 0 | 0 | $ \Sigma, +, a\rangle$ | u | 1 | a | s | $^3\Sigma_u^+$ | |
| $^4S + ^4S$ | 0 | 0 | 0 | $ \Sigma, +, s\rangle$ | g | 2, 0 | a | a | $^5\Sigma_g^+, ^1\Sigma_g^+$ | |
| | 0 | 0 | 0 | $ \Sigma, +, a\rangle$ | u | 3, 1 | s | a | $^7\Sigma_u^+, ^3\Sigma_u^+$ | |
| $^1P + ^1P$ | ± 1 | ± 1 | 2 | $ \Delta, +, s\rangle$ | g | 0 | s | s | $^1\Delta_g$ | |
| | ± 1 | ± 1 | 2 | $ \Delta, +, a\rangle$ | u | — | — | — | — | |
| | ± 1 | 0 | 1 | $ \Pi, +, s\rangle$ | g | 0 | s | s | $^1\Pi_g$ | |
| | ± 1 | 0 | 1 | $ \Pi, -, a\rangle$ | g | — | — | — | — | |
| | 0 | 0 | 1 | $ \Pi, -, s\rangle$ | u | 0 | s | s | $^1\Pi_u$ | |
| | 0 | 0 | 1 | $ \Pi, +, a\rangle$ | u | — | — | — | — | |
| | ± 1 | ∓ 1 | 0 | $ \Sigma, +, s\rangle$ | g | 0 | s | s | $^1\Sigma_g^+$ | |
| | ± 1 | ∓ 1 | 0 | $ \Sigma, -, a\rangle$ | g | — | — | — | — | |
| | ± 1 | ∓ 1 | 0 | $ \Sigma, -, s\rangle$ | u | 0 | s | s | $^1\Sigma_u^-$ | |
| | ± 1 | ∓ 1 | 0 | $ \Sigma, +, a\rangle$ | u | — | — | — | — | |
| | 0 | 0 | 0 | $ \Sigma, +, s\rangle$ | g | 0 | s | s | $^1\Sigma_g^+$ | |
| | 0 | 0 | 0 | $ \Sigma, +, a\rangle$ | u | — | — | — | — | |
| | $^2P + ^2P$ | ± 1 | ± 1 | 2 | $ \Delta, +, s\rangle$ | g | 0 | a | a | $^1\Delta_g$ |
| | | ± 1 | ± 1 | 2 | $ \Delta, +, a\rangle$ | u | 1 | s | a | $^3\Delta_u$ |
| ± 1 | | 0 | 1 | $ \Pi, +, s\rangle$ | g | 0 | a | a | $^1\Pi_g$ | |
| ± 1 | | 0 | 1 | $ \Pi, -, a\rangle$ | g | 1 | s | a | $^3\Pi_g$ | |
| ± 1 | | 0 | 1 | $ \Pi, -, s\rangle$ | u | 0 | a | a | $^1\Pi_u$ | |
| ± 1 | | 0 | 1 | $ \Pi, +, a\rangle$ | u | 1 | s | a | $^3\Pi_u$ | |
| ± 1 | | ∓ 1 | 0 | $ \Sigma, +, s\rangle$ | g | 0 | a | a | $^1\Sigma_g^+$ | |
| ± 1 | | ∓ 1 | 0 | $ \Sigma, -, a\rangle$ | g | 1 | s | a | $^3\Sigma_g^-$ | |
| ± 1 | | ∓ 1 | 0 | $ \Sigma, -, s\rangle$ | u | 0 | a | a | $^1\Sigma_u^-$ | |
| ± 1 | | ∓ 1 | 0 | $ \Sigma, +, a\rangle$ | u | 1 | s | a | $^3\Sigma_u^+$ | |
| 0 | | 0 | 0 | $ \Sigma, +, s\rangle$ | g | 0 | a | a | $^1\Sigma_g^+$ | |
| 0 | | 0 | 0 | $ \Sigma, +, a\rangle$ | u | 1 | s | a | $^3\Sigma_u^+$ | |

combinations $^3S + ^3S$, $^4S + ^4S$, $^1P + ^1P$ and $^2P + ^2P$ are explicitly worked out and the details are summarised in table 2.

Appendix A

In this appendix, we explicitly show how the molecular inversion symmetry operation (\hat{I}) acts upon the H-L type functions constructed according to eq. (4). Let us refer to figure 1 where the position vectors of the quasi-electrons 1 and 2 are indicated, both in relation to

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the respective nuclei A and B as well as with respect to the geometric centre O about which the inversion \hat{I} is to be performed. It is convenient to refer the particle positions to the origin O and accordingly we write

$$\Psi_{\text{orb}}(1, 2, \Lambda, \pm, p) = \{\psi_{nLM}(\mathbf{r}_{1A})\psi_{nLM'}(\mathbf{r}_{2B}) \pm \psi_{nLM'}(\mathbf{r}_{1A})\psi_{nLM}(\mathbf{r}_{2B})\} \\ + p\{\psi_{nLM}(\mathbf{r}_{2A})\psi_{nLM'}(\mathbf{r}_{1B}) \pm \psi_{nLM'}(\mathbf{r}_{2A})\psi_{nLM}(\mathbf{r}_{1B})\}, \quad (\text{A1})$$

$$= \left\{ \psi_{nLM}\left(\mathbf{r}_1 + \frac{\mathbf{R}}{2}\right)\psi_{nLM'}\left(\mathbf{r}_2 - \frac{\mathbf{R}}{2}\right) \pm \psi_{nLM'}\left(\mathbf{r}_1 + \frac{\mathbf{R}}{2}\right)\psi_{nLM}\left(\mathbf{r}_2 - \frac{\mathbf{R}}{2}\right) \right\} \\ + p\left\{ \psi_{nLM}\left(\mathbf{r}_2 + \frac{\mathbf{R}}{2}\right)\psi_{nLM'}\left(\mathbf{r}_1 - \frac{\mathbf{R}}{2}\right) \pm \psi_{nLM'}\left(\mathbf{r}_2 + \frac{\mathbf{R}}{2}\right)\psi_{nLM}\left(\mathbf{r}_1 - \frac{\mathbf{R}}{2}\right) \right\}. \quad (\text{A2})$$

From figure 1, it is easy to verify that

$$\hat{I}\mathbf{r}_{1A} = \mathbf{r}_{1'A} = -\mathbf{r}_1 + \frac{\mathbf{R}}{2}; \quad \hat{I}\mathbf{r}_{2B} = \mathbf{r}_{2'B} = -\mathbf{r}_2 - \frac{\mathbf{R}}{2}, \\ \hat{I}\mathbf{r}_{2A} = \mathbf{r}_{2'A} = -\mathbf{r}_2 + \frac{\mathbf{R}}{2}, \quad \hat{I}\mathbf{r}_{1B} = \mathbf{r}_{1'B} = -\mathbf{r}_1 - \frac{\mathbf{R}}{2}. \quad (\text{A3})$$

Substitution of the results of (A3) into (A2) gives

$$\hat{I}\Psi_{\text{orb}}(1, 2, \Lambda, \pm, p) = \{\psi_{nLM}(\mathbf{r}_{1'A})\psi_{nLM'}(\mathbf{r}_{2'B}) \pm \psi_{nLM'}(\mathbf{r}_{1'A})\psi_{nLM}(\mathbf{r}_{2'B})\} \\ + p\{\psi_{nLM}(\mathbf{r}_{2'A})\psi_{nLM'}(\mathbf{r}_{1'B}) \pm \psi_{nLM'}(\mathbf{r}_{2'A})\psi_{nLM}(\mathbf{r}_{1'B})\}, \\ = \left\{ \psi_{nLM}\left(-\mathbf{r}_1 + \frac{\mathbf{R}}{2}\right)\psi_{nLM'}\left(-\mathbf{r}_2 - \frac{\mathbf{R}}{2}\right) \pm \psi_{nLM'}\left(-\mathbf{r}_1 + \frac{\mathbf{R}}{2}\right)\psi_{nLM}\left(-\mathbf{r}_2 - \frac{\mathbf{R}}{2}\right) \right\} \\ + p\left\{ \psi_{nLM}\left(-\mathbf{r}_2 + \frac{\mathbf{R}}{2}\right)\psi_{nLM'}\left(-\mathbf{r}_1 - \frac{\mathbf{R}}{2}\right) \pm \psi_{nLM'}\left(-\mathbf{r}_2 + \frac{\mathbf{R}}{2}\right)\psi_{nLM}\left(-\mathbf{r}_1 - \frac{\mathbf{R}}{2}\right) \right\}. \quad (\text{A4})$$

If we use the simple property $\psi_{nLM}(-\mathbf{r}) = (-)^L\psi_{nLM}(\mathbf{r})$ of the single particle wave function (1), (A4) becomes

$$\hat{I}\Psi_{\text{orb}}(1, 2, \Lambda, \pm, p) = (-)^{2L}\left\{ \left[\psi_{nLM}\left(\mathbf{r}_1 - \frac{\mathbf{R}}{2}\right)\psi_{nLM'}\left(\mathbf{r}_2 + \frac{\mathbf{R}}{2}\right) \right. \right. \\ \left. \pm \psi_{nLM'}\left(\mathbf{r}_1 - \frac{\mathbf{R}}{2}\right)\psi_{nLM}\left(\mathbf{r}_2 + \frac{\mathbf{R}}{2}\right) \right] + p\left[\psi_{nLM}\left(\mathbf{r}_2 - \frac{\mathbf{R}}{2}\right)\psi_{nLM'}\left(\mathbf{r}_1 + \frac{\mathbf{R}}{2}\right) \right. \\ \left. \left. \pm \psi_{nLM'}\left(\mathbf{r}_2 - \frac{\mathbf{R}}{2}\right)\psi_{nLM}\left(\mathbf{r}_1 + \frac{\mathbf{R}}{2}\right) \right] \right\}, \quad (\text{A5})$$

$$= \pm p\Psi_{\text{orb}}(1, 2, \Lambda, \pm, p). \quad (\text{A6})$$

Since $(-)^{2L} = +1$, (A6) follows immediately by comparison of (A5) with (A2). In more explicit terms (A6) states that $\Psi_{\text{orb}}(1, 2, \Lambda, +, s)$ and $\Psi_{\text{orb}}(1, 2, \Lambda, -, a)$ are invariant under the symmetry operation \hat{I} , and thus of 'g' type while $\Psi_{\text{orb}}(1, 2, \Lambda, +, a)$ and $\Psi_{\text{orb}}(1, 2, \Lambda, -, s)$ change sign under \hat{I} and thus should carry the label 'u'.

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