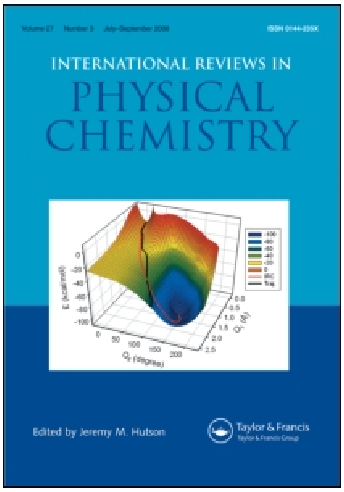

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The generalized Heitler–London theory for interatomic interaction and surface integral method for exchange energy

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Based on the theory of the permutation group and the Rayleigh–Schrödinger perturbation theory, a systematic procedure is developed for the calculation of interatomic potentials. When this method is applied to the H_2 molecule, the triplet (t) and singlet (s) energies are given by

$$E_{t,s} = \sum_{n=0}^{N} \varepsilon_n + \left(\sum_{n=0}^{N-1} s_n \pm 1 \right) \varepsilon_x,$$

where ε_n and s_n are the nth-order polarization energy and overlap integral respectively, and ε_x is the exchange energy defined as $\varepsilon_x = (E_t - E_s)/2$. With $N = 1$, this expression is shown to be identical with the usual Heitler–London energy; therefore this method is called generalized Heitler–London (GHL) theory. When ε_x is expanded in terms of the Coulomb integral and the exchange integral, many previous symmetry-adapted perturbation theories are shown to be subsets of this expansion. The advantage of the GHL theory is that, instead of using the approximate exchange integrals, the exchange energy calculated from the surface integral method can be used directly. After a careful examination of the surface integral method for H_2^+ and H_2, the exchange energy in a multielectron diatomic system is shown to be equal to the exchange energy of a single electron pair times a constant which can be obtained from a simple counting procedure. According to this theory, the energy curves of van der Waals potentials depend only on the known dispersion coefficients, the amplitude of the asymptotic wavefunctions, and the ionization energy of the individual atoms. With a simple analytical expression, potentials of many different diatomic systems are predicted with a high degree of accuracy. The GHL theory is also applied to the triatomic H_3 system. Many previous semiempirical surfaces including the well known London–Eyring–Polanyi–Sato surface are examined in the light of the present result. In particular, the Cashion–Herschbach surface is shown to encompass far more information than previously recognized. The new theory now contains all the terms needed for an exact calculation.

Contents

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1. Introduction

The interatomic potential is of fundamental importance for understanding the static and the dynamic properties of gases, liquids and solids. The foundation of the theory of interatomic potentials was laid in the year of 1927. In that year the chemical bond of the singlet state of the H_2 molecule was successfully described by Heitler and London [1] using a symmetrized wavefunction. The calculation showed that the stabilization of the bond is provided by the exchange integral. The same calculation also demonstrated that the exchange integral is responsible for the repulsive potential of the triplet state. In the same year, Wang [2] pointed out that there is always a long-range attraction between any pair of atoms, which is now known as the dispersion energy and is due to the interaction of a dipole with an instantaneous induced dipole. This long-range attraction together with the exchange repulsion are the origin of the so-called van der Waals potential between systems which do not form a chemical bond. Thus the exchange integral plays an important role in both the chemical and the van der Waals potentials.

While the basic physics of the interatomic potentials has been clear, the precise determination, especially of the weak van der Waals potentials, is still very difficult. With the advent of computers, the interaction potentials can in principle be calculated exactly through the variational molecular orbital methods. Problems associated with correlation configurations and basis set superpositions, however, complicate such *ab initio* calculations [3]. Essentially the difficulties arise from the errors inherent in the subtraction of the enormous energies of the separated atoms from the only slightly different energy of the interacting atoms. In recent years, quantum Monte Carlo methods have been used with considerable success [4], but such calculations provide little insight into the physical processes underlying the interaction. These problems are avoided in a perturbation calculation in which the potential is obtained directly. However, the correct symmetrization of the wavefunction has in the past led to difficult formal problems [5].

The only perturbation scheme that can be carried out systematically and with relative ease is the unsymmetrized Rayleigh–Schrödinger perturbation theory also commonly known as the polarization approximation [6]. The second-order polarization energy expressed in terms of the $1/R$ expansion is the well known induction and/or dispersion series [7], which if corrected for charge overlap [8] provides an excellent description of the long-range attraction [9]. However, until recently, it was generally believed that the exchange repulsion cannot be obtained from this theory. Therefore a large amount of effort has been devoted to the development of the so-called symmetry-adapted perturbation expansion (for a comprehensive survey of the history of symmetry-adapted perturbation theory see [10]).

Quite independent of these developments, the direct calculation of the exchange energy by a surface integral was first independently proposed in early 1950's by Firsov [11] and Holstein [12] in connection with the H_2^+ problem. This theory is based on the physical concept of the single electron hopping back and forth between the two protons. Using this approach, Herring [13] and Landau and Lifshitz [14] obtained the correct asymptotic exchange energy of the hydrogen molecular ion. This method was subsequently extended to treat the exchange of two electrons [15]. With this method, Herring and Flicker [16] were the first to obtain the correct asymptotic exchange energy of the hydrogen molecule. Although Herring [13, 17] was guided by the physical picture of the electron flowing back and forth, he was able to prove rigorously with a mathematical theorem that the result is asymptotically exact. Later Smirnov and Chibisov [18] extended this method to the alkali dimers. The generalization of this method to multielectron systems was first carried out by Umanskii and Voronin [19]. In 1970, Duman and Smirnov [20] showed that the exchange energy of the multielectron system can be expressed as a product of the exchange energy of a single pair of electrons and an angular momentum factor to account for the equivalence of the valence electrons. Subsequently this approach was only pursued by Russian groups [21, 22] and only in a few instances [23, 24] in the western literature. Only recently have several groups [25–28] including our own [29, 30] analysed and further developed the surface integral method for the exchange energy.

The exchange energy is closely related to the exchange integral but they are not identical. There are important differences which can be best illustrated by an example. In the familiar form of the Heitler–London theory, the wavefunction Ψ_t of the triplet and the wavefunction Ψ_s of the singlet states of the H_2 molecule are given by (for example [31])

$$\Psi_t = \frac{1}{[2(1-s_0)]^{1/2}}(|\Phi_0\rangle - T(12)\,|\Phi_0\rangle), \tag{1}$$

$$\Psi_s = \frac{1}{[2(1+s_0)]^{1/2}}(|\Phi_0\rangle - T(12)\,|\Phi_0\rangle), \tag{2}$$

with

$$s_0 = \langle \Phi_0 | T(12)\,|\Phi_0\rangle, \tag{3}$$

where Φ_0 is given by the product of the undisturbed hydrogenic wavefunctions of atom A with electron 1 and atom B with electron 2

$$\Phi_0 = \phi_A(1)\,\phi_B(2). \tag{4}$$

The exchange of electron 1 and 2 is indicated by the transposition $T(12)$. Furthermore, for abbreviation we shall use the following notation:

$$T(12)\,|\Phi_0\rangle = |\phi_A(2)\,\phi_B(1)\rangle = |\Phi_0'\rangle. \tag{5}$$

Thus s_0 in equation (3) is the overlap integral. The corresponding triplet E_t and singlet E_s energies are

$$E_t = \varepsilon_0 + \frac{J-K}{1-s_0}, \tag{6}$$

$$E_s = \varepsilon_0 + \frac{J+K}{1+s_0}, \tag{7}$$

with

$$J = \langle \Phi_0 | V | \Phi_0\rangle, \tag{8}$$

$$K = \langle \Phi_0 | VT(12) | \Phi_0\rangle, \tag{9}$$

where the zeroth-order energy ε_0 is simply the sum of the energies of the two undisturbed atoms. With the perturbing Hamiltonian V, the integral J defined in equation (8) is commonly known as the Coulomb integral. The exchange integral K given by equation (9) is of dominant importance in this theory.

The exchange energy ε_x and the Coulomb energy ε_C are usually defined as

$$\varepsilon_x = \tfrac{1}{2}(E_t - E_s), \tag{10}$$

$$\varepsilon_C = \tfrac{1}{2}(E_t + E_s). \tag{11}$$

Putting equations (6) and (7) into equation (10), we have

$$\varepsilon_x = \frac{s_0 J - K}{1 - s_0^2}. \tag{12}$$

With equations (6), (7) and (12), it follows from equation (11) that

$$\varepsilon_C = \varepsilon_0 + \varepsilon_1 + s_0\,\varepsilon_x, \tag{13}$$

where we have used the fact that the first-order polarization energy ε_1 of the unsymmetrized perturbation theory (see section 2.3) is equal to the Coulomb integral J. It is to be noted that the Coulomb energy is not equal to the Coulomb integral, nor is the Coulomb energy equal to the polarization energy.

The exchange integral in equation (9) depends on the zeroth-order approximation of the wavefunction. For a higher order of approximation, the corresponding exchange integral will of course be different. Since it changes from order to order, it would be difficult to assign a physical meaning to the exchange integral. On the other hand, the exchange energy in equation (10) depends on the eigenenergies of the system. It is a definitive quantity and is fundamental for understanding not only covalent chemical bonding, but also charge exchange in atomic collisions [32] and magnetism in many-body systems [17]. From equation (12), it is seen that in this approximation the exchange integral is equal to the negative of the exchange energy when the overlap integral s_0 is equal to zero.

By taking the difference and the sum of equations (11) and (10), and using equation (13), the Heitler–London energies E_t and E_s can be expressed in terms of ε_x:

$$E_t = \varepsilon_0 + \varepsilon_1 + (s_0 + 1)\,\varepsilon_x, \tag{14}$$

$$E_s = \varepsilon_0 + \varepsilon_1 + (s_0 - 1)\,\varepsilon_x. \tag{15}$$

Based on the unsymmetrized perturbation theory, Tang and Toennies [33, 34] developed a generalized Heitler–London (GHL) theory. In this theory the energy expressions appear to be identical with equations (14) and (15), except that both the polarization energy and the overlap integral contain higher-order terms. The definition of the exchange energy ε_x remains the same as given by equation (10).

In the next section, the GHL equation is developed from the viewpoint of the group theory. The advantage of the group theory approach is that the proper symmetry required by the Pauli principle of the electron exchange is built into the formulation. This is especially important for the systematic development of the theory for polyatomic systems.

In section 3, many symmetry-adapted perturbation theories (SAPTs) [35], such as those of Heitler–London [1], Murrell–Shaw (MS) [36], Musher–Amos (MA) [37], Jeziorski *et al.* [38] and Hirschfelder–Silbey [39], are shown to be subsets of the solutions of the GHL equation when it is expanded in terms of exchange integrals. The energy expressions obtained from the GHL equation are often more compact and transparent than those originally appearing in the SAPT.

A great advantage of the GHL theory is that the exchange energy obtained from the surface integral method can be used directly. After a careful examination of the exchange in H_2^+ and H_2, the surface integral methods for the exchange energy in multielectron ionic and neutral diatomic systems are reviewed in section 4. The coupling constant of Duman and Smirnov [20] is rederived and the original result is shown to be incorrect. The correct result is shown to be equal to the number of possible exchanges between the valence electrons with the same spin in the two atoms. In principle the surface integral method can be used to calculate the exchange energy for all interatomic distances. It is particularly useful in the asymptotic region, where the exchange energy can be expressed analytically.

In section 5, we first show that the potential of the chemical bond can be calculated by the GHL theory. However, it is for calculating the van der Waals potential that the GHL theory is most powerful. For many systems, the range of validity of the aysmptotic exchange energy expression includes the well region of the van der Waals potential. For these systems, the potentials predicted by the GHL theory are remarkably accurate. The GHL theory also naturally leads to the Tang–Toennies potential model which enables us to calculate a wide range of potentials of different systems with a universal analytical expression.

Another difference between the energies expressed in terms of the exchange integral and in terms of the exchange energy is that the denominator in equations (6) and (7) becomes a part of an additive term in equations (14) and (15). This is also the difference between the SAPT and the GHL theory. Without the factor $1 \pm s_0$ in the denominator, the GHL theory offers some conceptual and computational simplifications, especially when it is applied to polyatomic systems. In section 6, the GHL theory is developed for the all-important H_3 potential surface as a specific example. Many previous semiempirical surfaces for this system including the well known London–Eyring–Polanyi–Sato (LEPS) surface are examined in the light of the present results. In particular, the Cashion–Herschbach [40] surface is shown to encompass far more information than previously recognized. The new theory now contains all the terms needed for an exact calculation.

The paper closes with some concluding remarks in section 7. In this paper, the Born–Oppenheimer approximation neglecting the nuclear motion is assumed to be valid, and atomic units are used unless otherwise specified.

2. Group theory and generalized Heitler–London equation

Since the electrons are indistinguishable particles and have to obey the Pauli exclusion principle, the solution of the electronic Schrödinger equation must be properly symmetrized. The symmetrization of the wavefunction, while absolutely necessary, makes the problem considerably more complicated. Group theory [41, 42] is a natural tool for the purpose of reducing the complication to its simplest level. Through its irreducible representations, the matrix elements of the Hamiltonian are decoupled as far as possible. An n-electron system will be an invariant under the transformation of the S_n symmetry group. In this section, we shall first list some well known elements of the symmetry group [43, 44] for the clarification of the notation. Then we shall transform the Schrödinger equation into a GHL equation. The elaboration of this equation will start in the next section.

2.1. *Group theory and quantum mechanics* [41]

Let G be a group

$$G = \{g_1, g_2, \cdots, g_N\}, \tag{16}$$

where N is the order of the group. In the case of the symmetry group S_n, $N = n!$. It is understood that the first element g_1 is the identity I. Furthermore, let $D^\alpha(g)$, $\alpha = 1, 2, \cdots$ be the irreducible unitary matrix representations of g. Then they satisfy the following orthogonal conditions:

$$\sum_g D_{ij}^{*\alpha}(g)\, D_{i'j'}^{\alpha'}(g) = \frac{N}{n_\alpha} \delta_{\alpha\alpha'} \delta_{ii'} \delta_{jj'} \tag{17}$$

and

$$\sum_{\alpha=1}^{n_D} \sum_{i=1}^{n_\alpha} \sum_{j=1}^{n_\alpha} \frac{n_\alpha}{N} D_{ij}^{*\alpha}(g)\, D_{ij}^{\alpha}(g') = \delta_{gg'}, \tag{18}$$

where n_D denotes the number of different irreducible representations, n_α is the dimension of the representation α, and D^* denotes the complex conjugate of D.

For each element of the group, there is a unitary operator $T(g)$ which is an operator representation of g. For example, the permutation operators are the representations of the symmetry group of identical particles. Functions transform under a symmetry operation in accordance with an irreducible representation are basis functions of the representation. That is, if $\{u^{\alpha}_{ip}\}$ are the basis functions of the representation α, then

$$T(g)\, u^{\alpha}_{ip} = \sum_{j} u^{\alpha}_{jp}\, D^{\alpha}_{ji}(g). \tag{19}$$

For each representation, a set of projection operators can be defined with the aid of the irreducible matrix representations

$$P^{\alpha}_{ij} = \frac{n_{\alpha}}{N} \sum_{g} D^{*\alpha}_{ij}(g)\, T(g). \tag{20}$$

Through these projection operators, basis functions can be generated from a single function F:

$$u^{\alpha}_{ij} = P^{\alpha}_{ij} F. \tag{21}$$

Furthermore, it can be shown that

$$F = \sum_{\alpha} \sum_{j} u^{\alpha}_{jj}. \tag{22}$$

If the Hamiltonian H of a system is invariant under the symmetry operations $T(g)$ of the group, then its eigenfunctions must also transform in accordance with the irreducible representation of the group. In general the eigenfunction is a basis function if the representation is one dimensional. If the dimension is greater than one, the basis functions can be formed by a linear combination of the eigenfunctions belonging to that representation. In addition, the matrix elements of the Hamiltonian with respect to the basis functions must satisfy Wigner's theorem [41, 45]:

$$\langle u^{\alpha}_{ij} | H | u^{\alpha'}_{i'j'} \rangle = \delta_{ii'} \delta_{\alpha\alpha'} H^{\alpha}_{jj'}. \tag{23}$$

2.2. *Generalized Heitler–London equation*

To find the equation that governs the function F that will project out a set of basis functions which are linear combinations of the eigenfunctions, we first assume that we have at our disposal a set of basis functions $\{u^{\alpha}_{ij}\}$ that are already linear combinations of the eigenfunctions. By equation (22), we can write

$$HF = \sum_{\alpha} \sum_{j} H u^{\alpha}_{jj}. \tag{24}$$

Furthermore, with equations (21) and (20), u^{α}_{jp} can be projected out from F:

$$u^{\alpha}_{jp} = P^{\alpha}_{jp} F = \frac{n_{\alpha}}{N} \sum_{g} D^{*\alpha}_{jp}(g)\, T(g)\, F. \tag{25}$$

Without losing generality, $\{u^{\alpha}_{jp}\}$ can be taken as already orthonormalized [46]. Using the Wigner theorem of equation (23), we have

$$H u^{\alpha}_{jj} = \sum_{p} H^{\alpha}_{pj}\, u^{\alpha}_{jp}, \tag{26}$$

therefore

$$HF = \sum_{\alpha} \sum_{j} \sum_{p} H^{\alpha}_{pj}\, u^{\alpha}_{jp}. \tag{27}$$

Substituting equation (25) into equation (27), we obtain

$$HF = \sum_{g} \varepsilon_g T(g) F, \tag{28}$$

where

$$\varepsilon_g = \frac{1}{N} \sum_{\alpha} \sum_{j} \sum_{p} n_\alpha H^{\alpha}_{pj} D^{*\alpha}_{jp}(g). \tag{29}$$

Thus in order for the 'primitive' function F to be able to generate basis functions that are linear combinations of the eigenfunctions, it must satisfy equation (28). In the next section we shall show that, in the case of the H_2 molecule, this equation is identical with the GHL equation of Tang and Toennies [33, 34]. Therefore we shall designate equation (28) with the same name, but with the advantage that it can be applied to polyatomic systems. It is natural to call the quantity ε_g associated with $T(g)$ the generalized exchange energy. For example, if $T(g)$ interchanges particles 1 and 2, then ε_g is called the exchange energy ε_{12}. In the case of the H_2 molecule, ε_{12} happens to be the negative of the exchange energy ε_x defined in equation (10). The energy ε_I associated with the identity operation is called the Coulomb energy, in accordance with equation (11).

If ε_g can be independently calculated, the matrix elements of the Hamiltonian can be obtained from equation (29) in the following way. Multiplying $D^{\alpha}_{jp}(g)$ on both sides of equation (29) and summing over g, it follows from the orthogonal condition of equation (17) that

$$H^{\alpha}_{pj} = \sum_{g} D^{\alpha}_{jp}(g) \varepsilon_g. \tag{30}$$

The eigenvalues can then be obtained by diagonalizing this matrix.

2.3. *Unsymmetrized perturbation method and the generalized Heitler–London theory*

If the total Hamiltonian is divided as

$$H = H_0 + V, \tag{31}$$

the equation in the unsymmetrized Rayleigh–Schrödinger perturbation (polarization) theory [47, 48] given by

$$(H_0 + \lambda V) F = E_p F \tag{32}$$

is solved by first expanding the wavefunction and the energy according to

$$F = \sum_{n=0} \lambda^n \Phi_n, \tag{33}$$

$$E_p = \sum_{n=0} \lambda^n \varepsilon_n. \tag{34}$$

The different orders of the polarization wavefunctions satisfy the following set of equations:

$$(H_0 - \varepsilon_0) \Phi_0 = 0, \tag{35}$$

$$(H_0 - \varepsilon_0) \Phi_1 + (V - \varepsilon_1) \Phi_0 = 0, \tag{36}$$

and, for $n \geqslant 2$,

$$(H_0 - \varepsilon_0) \Phi_n + (V - \varepsilon_1) \Phi_{n-1} = \sum_{i=2}^{n} \varepsilon_i \Phi_{n-i}, \tag{37}$$

with the condition

$$\langle \Phi_0, \Phi_n \rangle = \delta_{n,0}. \tag{38}$$

The zeroth-order energy is simply the eigenvalue of H_0 and the higher-order energies are given by

$$\varepsilon_{n+1} = \langle \Phi_0, V\Phi_n \rangle. \tag{39}$$

We assume all the expansion series converge even for $\lambda = 1$ [49]; thus

$$HF = E_{\mathrm{p}} F, \tag{40}$$

and

$$E_{\mathrm{p}} = \sum_{n=0} \varepsilon_n, \tag{41}$$

$$F = \sum_{n=0} \Phi_n. \tag{42}$$

Equating equations (40) and (28), we have

$$E_{\mathrm{p}} F = \sum_g \varepsilon_g T(g) F. \tag{43}$$

Forming the inner product with $\langle \Phi_0 |$, and using the orthogonal condition of equation (38), this equation becomes

$$\sum_{n=0} \varepsilon_n = \varepsilon_I + \sum_{g \neq I} \sum_{n=0} \varepsilon_g \langle \Phi_0, T(g) \Phi_n \rangle. \tag{44}$$

The eigenenergies can then be obtained from this equation. Thus, the GHL theory consists of two parts. First the Schrödinger equation is solved by the unsymmetrized Rayleigh–Schrödinger perturbation method; then the proper symmetry is imposed by requiring the solution to satisfy the GHL equation. These procedures will become more transparent in the next section where we apply this theory to the H_2 molecule as a specific example.

3. The generalized Heitler–London and symmetry-adapted perturbation theories

We shall apply the theory developed in the last section to the H_2 molecule as a specific example. We shall see that the first-order energy reduces to the Heitler–London energy. Higher-order energies of many SAPTs are shown to be subsets of the solutions of the GHL equation. In addition the theory shows how to make use of the exchange energy obtained from the surface integral for the total energy calculation.

A closely related problem is the H_2^+ molecular ion. Pauling [50] was the first to apply the Heitler–London theory to the H_2^+ system in 1928. Although, in this case, the approach is now commonly known as linear combination of atomic orbitals, the formalism is the same. Thus, if the singlet-state and triplet-state wavefunctions of the H_2 molecule are replaced by the *gerade* and *ungerade* state wavefunctions respectively of the H_2^+ molecular ion, all the formulae derived for H_2 are equally applicable to H_2^+. The specific results are of course different.

3.1. *Generalized Heitler–London theory for the H_2 molecule and the H_2^+ molecular ion*

In the case of H_2, the symmetry group is $S_2 = \{I, (12)\}$. This group has two irreducible representations A and B, and both are one dimensional:

$$D^A(I) = 1, \tag{45}$$

$$D^A(12) = 1, \tag{46}$$

and

$$D^B(I) = 1, \tag{47}$$

$$D^B(12) = -1. \tag{48}$$

Since both are one dimensional, the eigenfunctions are basis functions. Clearly the singlet symmetric state wavefunction Ψ_s is the basis function of the representation A, and the triplet antisymmetric state wavefunction Ψ_t that of the representation B. Therefore

$$H_{11}^{A} = \langle \Psi_s | H | \Psi_s \rangle = E_s, \tag{49}$$

$$H_{11}^{B} = \langle \Psi_t | H | \Psi_t \rangle = E_t. \tag{50}$$

For this system, the generalized exchange energy of equation (29) becomes

$$\varepsilon_g = \frac{1}{N} \sum_{\alpha = A,\, B} n_\alpha H_{11}^{\alpha} D_{11}^{\alpha}(g). \tag{51}$$

Since $N = 2$ and $n_A = n_B = 1$,

$$\varepsilon_I = \tfrac{1}{2}(E_s + E_t), \tag{52}$$

$$\varepsilon_{12} = \tfrac{1}{2}(E_s - E_t). \tag{53}$$

Thus equation (28) takes the form

$$HF = [\varepsilon_I + \varepsilon_{12} T(12)] F. \tag{54}$$

Comparing equations (52) and (53) with equations (10) and (11), we see that

$$\varepsilon_I = \varepsilon_C \tag{55}$$

and

$$\varepsilon_{12} = - \varepsilon_X. \tag{56}$$

With this notation, equation (54) is identical with the GHL equation of Tang and Toennies [33, 34] first derived in a more direct way. Now it is clear that the symmetry of the problem has been fully taken into account in this equation.

In analogy to equation (3), we define the nth-order overlap integral as

$$s_n = \langle \Phi_0 | T(12) | \Phi_n \rangle. \tag{57}$$

Using this notation, we can express equation (44) as

$$\sum_{n=0} \varepsilon_n = \varepsilon_C - \varepsilon_X \sum_{n=0} s_n. \tag{58}$$

From equations (52) and (53), it is clear that

$$E_s = \varepsilon_C - \varepsilon_X, \tag{59}$$

$$E_t = \varepsilon_C + \varepsilon_X. \tag{60}$$

Substituting ε_C from equation (58) into these equations, and truncating the summations in equations (41) and (42) at the Mth term, we obtain the eigenenergies of H_2 up to and including the Mth order:

$$E_s = \sum_{n=0}^{M} \varepsilon_n + \left(\sum_{n=0}^{M-1} s_n - 1 \right) \varepsilon_X, \tag{61}$$

$$E_t = \sum_{n=0}^{M} \varepsilon_n + \left(\sum_{n=0}^{M-1} s_n + 1 \right) \varepsilon_X. \tag{62}$$

For $M = 1$ they are identical with the Heitler–London energies of equations (14) and (15). Therefore these energies can be regarded as a generalization of the Heitler–London theory. The advantage of the GHL theory is that the exchange energy calculated from the surface integral method can be used directly for the eigenenergy computation. To make clear the difference between the exchange energy and the exchange integral, we shall first show that the various SAPTs using exchange integrals are subsets of the solutions of the GHL equation.

3.2. *Generalized Heitler–London equation and symmetry-adapted perturbation theories*

Putting equations (31) and (42) into equation (54), we obtain

$$(H_0 + V)\left|\sum_{n=0} \Phi_n\right\rangle = (\varepsilon_I + \varepsilon_{12}\, T(12))\left|\sum_{n=0} \Phi_n\right\rangle, \tag{63}$$

and, forming the inner product with $\langle \Phi_0|$, we have

$$\varepsilon_0 + \sum_{n=0} \langle \Phi_0 V \Phi_n \rangle = \varepsilon_I + \varepsilon_{12} \sum_{n=0} s_n, \tag{64}$$

where we have used equations (38) and (57).

In order to conform with the common usage and facilitate a systematic development, we shall first clarify some definitions. As shown in equations (8) and (39), the first-order energy is often called the Coulomb integral, we shall follow this convention and refer to Coulomb integrals of order $n+1$ defined by

$$J_{n+1} = \langle \Phi_0 V \Phi_n \rangle. \tag{65}$$

From equation (32), it is seen that V is associated with λ; therefore it is a first-order quantity. Since Φ_n is associate with λ^n and is nth order, equation (65) shows that J_{n+1} is indeed an $(n+1)$th-order quantity. Similarly we shall define the $(n+1)$th-order exchange integral as

$$K_{n+1} = \langle \Phi_0 V \Phi_n' \rangle, \tag{66}$$

where $\Phi_n' = T(12)\,\Phi_n$. The nth-order overlap integral of equation (57) is an nth-order quantity. We shall maintain this system of numbering the subscripts in the following development. Thus J and K as commonly defined in equations (8) and (9) are in fact J_1 and K_1 respectively. With this notation, equation (64) becomes

$$\varepsilon_0 + \sum_{n=1} J_n = \varepsilon_I + \varepsilon_{12} \sum_{n=0} s_n. \tag{67}$$

With the same notation as in equation (5), $T(12)\,H = H'$, the fact that the Hamiltonian is invariant with respect to the interchange of electrons is expressed as $H' = H$. With H_0' and V' similarly defined, it is clear that

$$H_0 + V = H_0' + V'. \tag{68}$$

Now let us return to equation (63). Forming the inner product by multiplying this time with the 'exchanged' wavefunction $\langle \Phi_0'|$ and using equations (38) and (68), we get

$$\left\langle \Phi_0' \left| H_0' + V' \right| \sum_{n=0} \Phi_n \right\rangle = \varepsilon_I \sum_{n=0} s_n + \varepsilon_{12}. \tag{69}$$

Since

$$\left\langle \Phi_0', H_0' \sum_{n=0} \Phi_n \right\rangle = \varepsilon_0 \sum_{n=0} s_n, \tag{70}$$

it follows from equation (69) and the definition of the exchange integrals that

$$\varepsilon_0 \sum_{n=0} s_n + \sum_{n=1} K_n = \varepsilon_I \sum_{n=0} s_n + \varepsilon_{12}. \tag{71}$$

Adding equation (71) to equation (67), we have

$$\varepsilon_0\left(1+\sum_{n=0} s_n\right)+\sum_{n=1}(J_n+K_n)=(\varepsilon_I+\varepsilon_{12})\left(1+\sum_{n=0} s_n\right). \tag{72}$$

Thus

$$\varepsilon_I+\varepsilon_{12}=\varepsilon_0+\frac{\sum_{n=1}(J_n+K_n)}{1+\sum_{n=0} s_n}. \tag{73}$$

Similarly, subtracting equation (71) from equation (67), we get

$$\varepsilon_I-\varepsilon_{12}=\varepsilon_0+\frac{\sum_{n=1}(J_n-K_n)}{1-\sum_{n=0} s_n}. \tag{74}$$

With $\varepsilon_I=\varepsilon_C$, $\varepsilon_{12}=-\varepsilon_x$ and equations (59) and (60), these are just the singlet and triplet energies. If the series is truncated at Nth term, we have

$$E_{\pm}^{N}=\varepsilon_0+\frac{\sum_{n=1}^{N}(J_n\pm K_n)}{1\pm\sum_{n=0}^{N-1} s_n}. \tag{75}$$

The upper sign is associated with the singlet state and the lower sign with the triplet state. As stated earlier, these formulae apply equally well to the H_2^+ molecule ion [33]. In that case, the upper sign is associate with the *gerade* state and the lower sign with the *ungerade* state.

For the first-order energy, we simply put $N=1$ in equation (75). The results are the usual Heitler–London energies of equations (6) and (7). With $N=2$, the second-order energy is contained in $E_{\pm}^{2}$, which includes the zeroth-, first- and second-order terms:

$$E_{\pm}^{2}=\varepsilon_0+\frac{(J_1+K_1)\pm(J_2+K_2)}{1\pm(s_0+s_1)}. \tag{76}$$

Since the first-order overlap s_1 is in the denominator, we make an expansion

$$[1\pm(s_0+s_1)]^{-1}=(1\pm s_0)^{-1}\left(1\mp\frac{s_1}{1\pm s_0}\cdots\right). \tag{77}$$

Substituting into equation (76) and keeping quantities equal to or less than second order, we obtain

$$E_{\pm,2}=\varepsilon_0+\frac{J_1\pm K_1}{1\pm s_0}+\frac{J_2+K_2}{1\pm s_0}\mp\frac{s_1}{1\pm s_0}\,\frac{J_1\pm K_1}{1\pm s_0}. \tag{78}$$

This result is identical with that obtained from the symmetry-adapted MS–MA [36, 37] perturbation theory. This equation is exactly the same as equations (10) and (11) of Chałasinski and Jeziorski [51], which were shown to contain terms up to third power in the zeroth-order overlap. The agreement between the two results is, in fact, not readily apparent [33, 52] since equations (10) and (11) of [51] appear to be much more complicated, but they can, with some effort, be shown to reduce to the same set of terms in equation (78).

In the present approach, equation (78) is obtained in a simple and direct way. The grouping of the terms follow naturally from the theory. The first two terms on the right are clearly the zeroth- and the first-order energy. The third term is a second-order energy, coming from the second-order Coulomb and exchange integrals. The last term is a coupling between the first-order energy and first-order overlap integral, making an additional contribution to the second-order energy.

We can obtain any order of energy by expanding equation (75) in a straightforward manner. For example, for the third-order energy we can expand

$$E_{\pm}^{3} = \varepsilon_0 + \frac{\sum_{n=1}^{3} (J_n \pm K_n)}{1 \pm \sum_{n=0}^{2} s_n} \tag{79}$$

and collect terms up to and including third-order quantities. The resulting third-order energy is

$$E_{\pm,3} = E_{\pm,2} + \frac{J_3 \pm K_3}{1 \pm s_0} \mp \frac{\sum_{i=1}^{2} s_i (J_{3-i} \pm K_{3-i})}{(1 \pm s_0)^2} + \frac{s_1^2 (J_1 \pm K_1)}{(1 \pm s_0)^3}, \tag{80}$$

where $E_{\pm,2}$ is given by equation (78). Obviously this process can be continued. Cwiok *et al.* [52] showed that the entire series of the symmetrized Rayleigh–Schrödinger expansion [38] can be generated this way.

An alternative approach to calculating the energy is based on the expectation value of the Hamiltonian [53]. This is the usual starting point in the variational method. For this purpose the wavefunction, which in the perturbation theory does not have to be normalized, must now be normalized. As mentioned earlier, the usual Heitler–London energy is the first-order energy from the perturbation calculation. It is also the first-order energy from the expectation value of the Hamiltonian. If the system does not involve exchange, the second-order perturbation energy will also be exactly the same as the second-order energy from the expectation value of the Hamiltonian. However, with the exchange this is not the case.

If the wavefunction is truncated after the first order, then

$$F = N(\Phi_0 + \Phi_1), \tag{81}$$

and the normalization constant N is given by the requirement

$$\langle F, F \rangle = 1. \tag{82}$$

Forming the inner product with the GLH equation of equation (54), first with $\langle F|$ and then with $\langle F'|$, one can show [33], following the same procedure as before, that the energies up to and including the second-order quantities are given by

$$\langle E_{\pm,2} \rangle = \varepsilon_0 + \frac{J_1 \pm K_1}{1 \pm s_0} + \frac{J_2 + K_2}{1 \pm s_0} \mp \frac{s_1}{1 \pm s_0} \left(\frac{2(J_1 \pm K_1)}{1 \pm s_0} - J_1 \right). \tag{83}$$

This expression is identical with the result of the expectation value [33]

$$\langle E_{\pm,2} \rangle = \langle \Psi_{\pm} | H | \Psi_{\pm} \rangle \tag{84}$$

with

$$|\Psi_{\pm}\rangle = N'(|\Phi_0 + \Phi_1\rangle \pm T(12)\,|\Phi_0 + \Phi_1\rangle), \tag{85}$$

where N' is the normalization constant. Comparing equation (83) with the second-order perturbation energy of equation (78), we see that the zeroth an first orders are identical; however, there is a small difference in the last term of the second order. Equation (83) is also the result found by McQuarrie and Hirschfelder [54] with the

Hirschfelder–Silbey exchange perturbation theory [39]. Again the original expression of [54] appears to be rather involved and looks quite different, but it has been shown [33] to reduce to the identical form of equation (83).

It is interesting to note that, although the second-order perturbation result generated from the GHL equation is identical with that of the MS–MA theory, the expectation value of GHL is different from the MS–MA theory. The expectation value of the MS–MA theory is a very poor approximation [53] because its first-order wavefunction is not symmetrized, whereas the expectation value of GHL is identical with that of Hirschfelder–Silbey theory [39] which gives reasonable numerical results [53].

Thus we have shown in this section that almost all SAPTs can be systematically generated from the GHL equation with polarization wavefunctions. The resulting experessions are often more compact than in those theories.

4. Surface integral method for exchange energy

4.1. *Exchange energy of H_2^+ by the surface integral method*

The Hamiltonian of H_2^+ written in the coordinates shown in figure 1 is

$$H = \tfrac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R}. \tag{86}$$

In this case, $T(12)$ represents the interchange of A and B. Clearly $T(12)H = H$. Therefore the eigenfunctions of this Hamiltonian must be either symmetric (*gerade*) or antisymmetric (*ungerade*). All formulae derived so far for H_2 are equally applicable provided that all quantities associated with the singlet (s) state is understood to be referring to the *gerade* (*g*) state, and those with the triplet (t) state, referring to the *ungerade* (*u*) state. Furthermore, instead of equation (4), Φ_0 is simply the hydrogenic wavefunction around A

$$\Phi_0 = \phi_A(r_a) = \frac{1}{\pi^{1/2}} \exp(-r_a), \tag{87}$$

and

$$T(12)\,\Phi_0 = \phi_B(r_b) = \frac{1}{\pi^{1/2}} \exp(-r_b). \tag{88}$$

If R is very large and initially we have an isolated hydrogen atom, the wavefunction is of course given by Φ_0. As soon as the other proton is taken into consideration, Φ_0 is no longer an eigenfunction because it does not have the necessary symmetry. This means the electron is not in a stationary state and has to move. To study the time development, we consider the linear combination

$$\Psi = \frac{1}{2^{1/2}} (\Psi_s \exp(-iE_s t) + \Psi_t \exp(-iE_t t)). \tag{89}$$

The density represented by this wavefunction is

$$\rho = \tfrac{1}{2}[|\Psi_s|^2 + \Psi_s^* \Psi_t \exp(-i\Delta t) + \Psi_s \Psi_t^* \exp(i\Delta t) + |\Psi_t|^2], \tag{90}$$

where $\Delta = E_t - E_s = 2\varepsilon_x$. At $t = 0$, equation (90) becomes

$$\rho(t = 0) = \tfrac{1}{2}|\Psi_s + \Psi_t|^2. \tag{91}$$

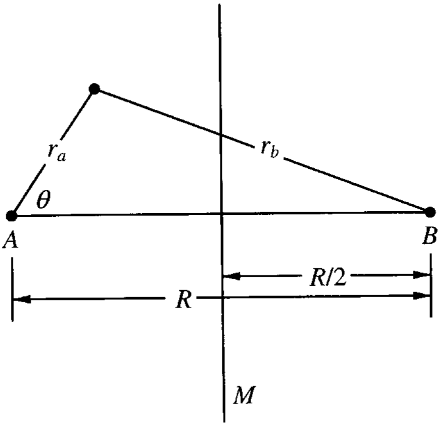

Figure 1. Electron and proton coordinates of the H_2^+ molecular ion. M is the median plane half-way between the two protons.

This is the density of the wavefunction

$$\Phi_a = \frac{1}{2^{1/2}}(\Psi_s + \Psi_t), \tag{92}$$

which, with the proper choice of phase, is localized around proton A. At $t = \pi/\Delta$, equation (90) gives

$$\rho\left(t = \frac{\pi}{\Delta}\right) = \tfrac{1}{2}|\Psi_s - \Psi_t|^2, \tag{93}$$

which is the density of a wavefunction

$$\Phi_b = \frac{1}{2^{1/2}}(\Psi_s - \Psi_t) \tag{94}$$

localized around B. The exchange has taken place. As time goes on, the electron oscillates between A and B with a frequency of Δ/h. In this process, the decrease in density around A must be equal to the total current flowing across the median plane M between A and B (see figure 1). That is

$$-\frac{\partial}{\partial t}\int_v \rho \, \mathrm{d}v = \int_s \mathbf{J}\cdot \mathrm{d}\mathbf{s}, \tag{95}$$

where

$$\mathbf{J} = \frac{\mathrm{i}}{2}(\Psi^* \nabla \Psi - \Psi \nabla \Psi^*). \tag{96}$$

If the volume integration is over the entire left side of M, the surface integral is over M. Without losing generality, Ψ_s and Ψ_t can be taken as real. Using equation (90), we find that the left-hand side of equation (95) is

$$-\frac{\partial}{\partial t}\int_v \rho \, \mathrm{d}v = \Delta \sin(\Delta t)\int_{\text{left}} \Psi_s \Psi_t \, \mathrm{d}v. \tag{97}$$

With equations (89) and (96), the right-hand side of equation (95) is given by

$$\int_s \mathbf{J}\cdot \mathrm{d}\mathbf{s} = \tfrac{1}{2}\sin(\Delta t)\int_M (\Psi_t \nabla \Psi_s - \Psi_s \nabla \Psi_t)\cdot \mathrm{d}\mathbf{s}. \tag{98}$$

Therefore equation (95) becomes

$$\Delta \int_{\text{left}} \Psi_s \Psi_t \, dv = \frac{1}{2} \int_M (\Psi_t \nabla \Psi_s - \Psi_s \nabla \Psi_t) \cdot d\mathbf{s}. \tag{99}$$

This is an identity. It can of course also be derived from the time-independent Schrödinger equation [55]; however, the physics would be less transparent. With Φ_a and Φ_b given by equations (92) and (94) respectively and $\Delta = 2\varepsilon_x$, equation (99) can be written as

$$\varepsilon_x \int_{\text{left}} \Psi_s \Psi_t \, dv = \frac{1}{4} \int_M (\Phi_a \nabla \Phi_b - \Phi_b \nabla \Phi_a) \cdot d\mathbf{s}. \tag{100}$$

At any point on the median plane M,

$$\Phi_b = \Phi_a, \tag{101}$$

$$\nabla \Phi_b \cdot d\mathbf{s} = - \nabla \Phi_a \cdot d\mathbf{s}; \tag{102}$$

therefore

$$\int_M (\Phi_a \nabla \Phi_b - \Phi_b \nabla \Phi_a) \cdot d\mathbf{s} = - 2 \int_M \Phi_a \nabla \Phi_a \cdot d\mathbf{s}. \tag{103}$$

Furthermore by direct substitution,

$$\int_{\text{left}} \Psi_s \Psi_t \, dv = \frac{1}{2} \int_{\text{left}} (\Phi_a^2 - \Phi_b^2) \, dv. \tag{104}$$

Since Φ_a and Φ_b are normalized and are symmetrical with respect to the median plane,

$$\int_{\text{left}} (\Phi_a^2 - \Phi_b^2) \, dv = 1 - 2 \int_{\text{right}} \Phi_a^2 \, dv. \tag{105}$$

Therefore it follows from equation (100) that

$$\varepsilon_x = \frac{- \int_M \Phi_a \nabla \Phi_a \cdot d\mathbf{s}}{1 - 2 \int_{\text{right}} \Phi_a^2 \, dv}. \tag{106}$$

This expression is exact. The numerator is identical with the asymptotic exchange energy of Herring [13].

4.2. *Exchange energy of H_2 by the surface integral method*

In this section we shall derive a similar formula to equation (106) for the exchange energy of the H_2 molecule [56]. For the one-electron problem of H_2^+, it is clear that the median plane M divides the space into two parts, and the exchange can be interpreted as resulting from the electron flowing back and forth across this plane. Now, for the two electron H_2 problem, we must first carefully examine what is meant by electron exchange. We shall start with a one-dimensional problem, since it is conceptually simpler. The ideas developed will be useful for the real three-dimensional problem.

Let the two protons and the two electrons all lie on a line. Electron 1 is initially associated with proton A, and electron 2 with proton B, as shown in figure 2(*a*). The coordinates z_1 and z_2 are measured from the centre of the system. Proton A is located at $z_A = - R/2$, and proton B at $z_B = R/2$. If electron 1 goes to the right of electron 2, as shown in figure 2(*b*), we say that the exchange has occurred. Clearly exchange takes place at $z_1 = z_2$.

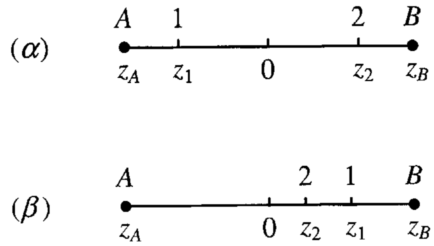

Figure 2. Coordinates used to discuss the two-electron exchange in a simple one-dimensional model. (α) The two electrons are with 'their own' protons. (β) The exchange has taken place.

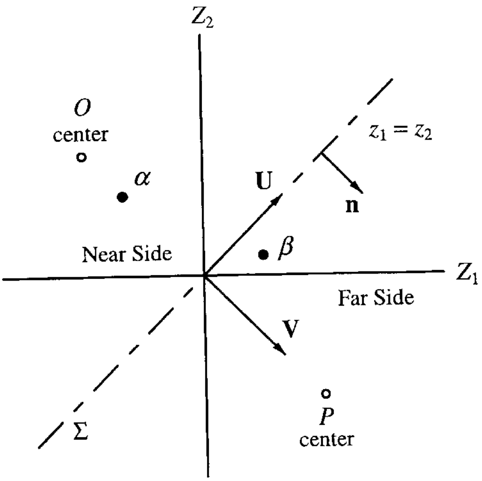

Figure 3. Two-dimensional configuration used to describe the one-dimensional exchange in figure 2. The exchange is represented by the 'home-based' wavefunction flowing from the near side to the far side.

This one-dimensional exchange can be expressed in the two-dimensional configuration space as shown in figure 3. Each point in this space represents the positions of the two electrons. Following Herring [13], the point O is called the 'original centre'. It is the position where electron 1 coincide with proton A and electron 2 with proton B. The 'P centre' is the point obtained from the original centre by applying the permutation to the electronic coordinates. Thus a wavefunction which is large near the original centre and small elsewhere represents the fact that electron 1 is essentially localized around A and electron 2 around B. Herring calls this a 'home-based function'. Similarly, a wavefunction which is large near the P centre represents the electron 2 localized around A and 1 around B.

Let us call the upper left half-plane the 'near side' and the lower right half-plane the 'far side'. Anywhere in the near side, the distance to the original centre is smaller than that to the P centre; therefore the electrons belong to their 'original' protons. The electron exchange is represented by the flux of the home-based function flowing through the line $z_1 = z_2$ from the near side to the far side.

In this configuration space, the distance from a representative point to the original centre is

$$d_o = [(z_1 - z_A)^2 + (z_2 - z_B)^2]^{1/2} \tag{107}$$

and to the P centre is

$$d_P = [(z_1 - z_B)^2 + (z_2 - z_A)^2]^{1/2}. \tag{108}$$

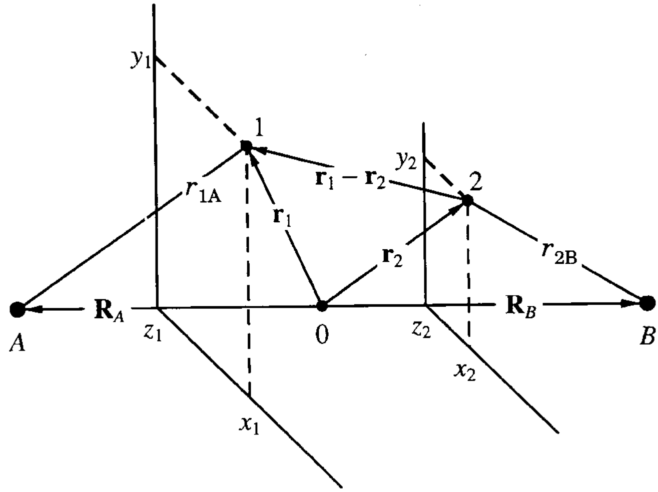

Figure 4. Three-dimensional coordinates used to calculate the surface and volume integrals for the two electron exchange energy.

The electrons are with their own protons if $d_o < d_p$, and the exchange has already occurred if $d_o > d_p$, and the exchange takes place at $d_o = d_p$. With the help of equations (107) and (108), this last condition can be expressed as

$$(z_1 - z_A)^2 + (z_2 - z_B)^2 - (z_1 - z_B)^2 - (z_2 - z_A)^2 = 0. \tag{109}$$

After rearranging, this equation becomes

$$2(z_1 - z_2)(z_A - z_B) = 0; \tag{110}$$

since z_A and z_B are fixed, this means that $z_1 = z_2$ as expected.

In three dimensions, we define the electron exchange in a similar way. We use the same criteria to decide whether the exchange has taken place. However, all distances must now be defined in terms of position vectors. If we consider $(\mathbf{r}_1, \mathbf{r}_2) = (x_1, y_1, z_1, x_2, y_2, z_2)$ as a six-dimensional configuration space, then the point $(\mathbf{R}_A, \mathbf{R}_B)$ is the original centre, and $(\mathbf{R}_B, \mathbf{R}_A)$ the P centre. Corresponding to equations (107) and (108), the distances to the original centre and to the P centre are respectively

$$d_o = (|\mathbf{r}_1 - \mathbf{R}_A|^2 + |\mathbf{r}_2 - \mathbf{R}_B|^2)^{1/2} \tag{111}$$

and

$$d_p = (|\mathbf{r}_1 - \mathbf{R}_B|^2 + |\mathbf{r}_2 - \mathbf{R}_A|^2)^{1/2}. \tag{112}$$

Similarly equation (109), which defines the boundary between the near and far side of the configuration space of the one-dimensional exchange, can be taken over directly. Written in terms of the coordinates shown in figure 4, this equation becomes

$$|\mathbf{r}_1 - \mathbf{R}_A|^2 + |\mathbf{r}_2 - \mathbf{R}_B|^2 - |\mathbf{r}_1 - \mathbf{R}_B|^2 - |\mathbf{r}_2 - \mathbf{R}_A|^2 = 0. \tag{113}$$

It can be shown that equation (113) is indeed a five-dimensional hyperplane which divides the six-dimensional configuration space into two equal and simply connected parts. After rearranging, this equation can be written as

$$2(\mathbf{r}_1 - \mathbf{r}_2)\cdot(\mathbf{R}_B - \mathbf{R}_A) = 0. \tag{114}$$

Since this is a dot product, this equation simply says that the vector $\mathbf{r}_1 - \mathbf{r}_2$ is perpendicular to $\mathbf{R}_B - \mathbf{R}_A$, which is the vector going from A to B. Thus this five dimensional hyperplane, which we shall designate as Σ, corresponds to all planes

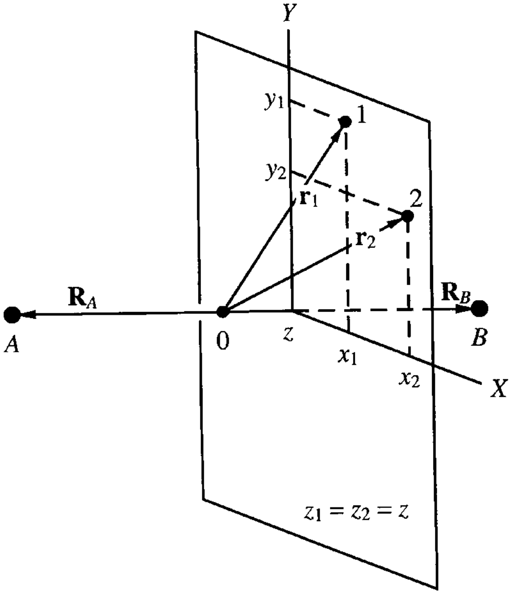

Figure 5. Coordinates of one of the possible planes perpendicular to the inter-nuclear axis AB. All the planes similar to this make up the five-dimensional hyperplane Σ dividing the six-dimensional configuration space of the two electrons into the near side and far side.

perpendicular to the line AB in three dimensions. One of them is shown in figure 5. If we use the line AB as the z axis, then clearly on these planes $z_1 = z_2$.

We call that part of the space containing the original centre the near side, and the part with the P centre the far side. The home-based wavefunction in this six-dimensional configuration space is a function essentially localized around the original centre. The flux of this function flowing across the five dimensional hyperplane Σ from the near side to the far side represents the process of electron exchange.

With these understandings, we can derive the exchange energy of H_2 in almost exactly the same way as that of H_2^+. Every equation starting from equation (89) can be taken over directly for this case, provided that it is understood that the gradient ∇ operates on both electrons

$$\nabla = (\nabla_1, \nabla_2). \tag{115}$$

Written in this six-dimensional space, equation (100) takes the form

$$\varepsilon_x \int_{\text{near}} \Psi_s \Psi_t \, d^6 r = \frac{1}{4} \int_{\Sigma} (\Phi_a \nabla \Phi_b - \Phi_b \nabla \Phi_a) \cdot \mathbf{n} \, d^5 s, \tag{116}$$

where the volume integral is over the entire near side and the surface integral is over the five-dimensional hyperplane Σ with a unit normal **n** directing from the near side to the far side.

We can use the coordinates $(x_1, y_1, z_1, x_2, y_2, z_2)$ to evaluate these integrals. To describe the boundary planes, it is convenient to define

$$u = \frac{1}{2^{1/2}}(z_1 + z_2), \tag{117}$$

$$v = \frac{1}{2^{1/2}}(z_1 - z_2). \tag{118}$$

This transformation represents a rotation of 45° as shown in figure 3. As mentioned earlier, on the boundary planes z_1 is equal to z_2, $z_1 = z_2$. This means that on Σ, $v = 0$. Everywhere in the near side $v < 0$, and in the far side $v > 0$.

With these coordinates, it is easy to show, in analogy to equations (104) and (105), that

$$\int_{\text{near}} \Psi_{\text{s}}\, \Psi_{\text{t}}\, \mathrm{d}^6 r = \frac{1}{2}\left(1 - 2\int_{\text{far}} \Phi_{\text{a}}^2\, \mathrm{d}^6 r\right). \tag{119}$$

However, there is a difference in the surface integral which requires some explanation. First we note that in this case

$$\begin{aligned} \Phi_{\text{a}}(\mathbf{r}_2, \mathbf{r}_1) &= \Psi_{\text{s}}(\mathbf{r}_2, \mathbf{r}_1) + \Psi_{\text{t}}(\mathbf{r}_2, \mathbf{r}_1) \\ &= \Psi_{\text{s}}(\mathbf{r}_1, \mathbf{r}_2) - \Psi_{\text{t}}(\mathbf{r}_1, \mathbf{r}_2) \\ &= \Phi_{\text{b}}(\mathbf{r}_1, \mathbf{r}_2), \end{aligned} \tag{120}$$

which means

$$\Phi_{\text{a}}(x_2, y_2, x_1, y_1, u, -v) = \Phi_{\text{b}}(x_1, y_1, x_2, y_2, u, v). \tag{121}$$

The surface element of Σ is

$$\mathrm{d}^5 s = \mathrm{d}x_1\, \mathrm{d}y_1\, \mathrm{d}x_2\, \mathrm{d}y_2\, \mathrm{d}u,$$

and the gradient in the direction of $\mathbf{n}$ on Σ is given by

$$\begin{aligned} \nabla\Phi_{\text{a}} \cdot \mathbf{n} &= [\nabla\Phi_{\text{a}}(x_1, y_1, x_2, y_2, u, v) \cdot \mathbf{n}]_{v=0} \\ &= \left[\frac{\partial}{\partial v}\Phi_{\text{a}}(x_1, y_1, x_2, y_2, u, v)\right]_{v=0} \end{aligned} \tag{122}$$

and

$$\begin{aligned} \nabla\Phi_{\text{b}} \cdot \mathbf{n} &= [\nabla\Phi_{\text{a}}(x_2, y_2, x_1, y_1, u, -v) \cdot \mathbf{n}]_{v=0} \\ &= \left[\frac{\partial}{\partial v}\Phi_{\text{a}}(x_2, y_2, x_1, y_1, u, -v)\right]_{v=0} \\ &= \left[-\frac{\partial}{\partial v}\Phi_{\text{a}}(x_2, y_2, x_1, y_1, u, v)\right]_{v=0}. \end{aligned} \tag{123}$$

Therefore

$$\int_{\Sigma} \Phi_{\text{a}}\, \nabla\Phi_{\text{b}} \cdot \mathbf{n}\, \mathrm{d}^5 s = -\int_{\Sigma} \Phi_{\text{b}}(x_2, y_2, x_1, y_1, u, 0)\left[\frac{\partial}{\partial v}\Phi_{\text{a}}(x_2, y_2, x_1, y_1, u, v)\right]_{v=0} \mathrm{d}^5 s \tag{124}$$

and

$$\int_{\Sigma} \Phi_{\text{b}}\, \nabla\Phi_{\text{a}} \cdot \mathbf{n}\, \mathrm{d}^5 s = \int_{\Sigma} \Phi_{\text{b}}(x_1, y_1, x_2, y_2, u, 0)\left[\frac{\partial}{\partial v}\Phi_{\text{a}}(x_1, y_1, x_2, y_2, u, v)\right]_{v=0} \mathrm{d}^5 s. \tag{125}$$

The integration over $x_1 y_1$ and $x_2 y_2$ are all from $-\infty$ to ∞ and can be interchanged; hence

$$\int_{\Sigma} \Phi_{\text{a}}\, \nabla\Phi_{\text{b}} \cdot \mathbf{n}\, \mathrm{d}^5 s = -\int_{\Sigma} \Phi_{\text{b}}\, \nabla\Phi_{\text{a}} \cdot \mathbf{n}\, \mathrm{d}^5 s. \tag{126}$$

Therefore it follows from equations (116) and (119) that

$$\varepsilon_{\text{x}}\left(1 - 2\int_{\text{far}} \Phi_{\text{a}}^2\, \mathrm{d}^6 r\right) = -\int_{\Sigma} \Phi_{\text{b}}\, \nabla\Phi_{\text{a}} \cdot \mathbf{n}\, \mathrm{d}^5 s$$

or

$$\varepsilon_{\text{x}} = \frac{-\int_{\Sigma}(T(12)\,\Phi_{\text{a}})\,\nabla\Phi_{\text{a}} \cdot \mathbf{n}\, \mathrm{d}^5 s}{1 - 2\int_{\text{far}} \Phi_{\text{a}}^2\, \mathrm{d}^6 r}. \tag{127}$$

Formally equation (127) is almost identical with equation (106), except that Φ_a is replaced by $T(12)\,\Phi_a$.

4.3. *Zeroth-order exchange energy of H_2^+ and H_2*

To evaluate the exchange energy by the surface integral method, we need the localized wavefunction. The simplest approximation is of course the undisturbed zeroth-order atomic orbital. For the H_2^+ ion, substituting

$$\Phi_0 = \frac{1}{\pi^{1/2}} \exp(r_a) \tag{128}$$

as Φ_a into the exchange energy expression of equation (106), both the numerator and the denominator can be easily evaluated [57]; the result is

$$\varepsilon_x = \frac{(R/2)\exp(-R)}{1-[(R/2)+1]\exp(-R)}. \tag{129}$$

This expression is to be compared with the Heitler–London result

$$\varepsilon_x^{HL} = \frac{(2R/3-1/R)\exp(-R)+(1+1/R)(1+R+R^2/3)\exp(-3R)}{1-(1+R+R^2/3)^2\exp(-2R)}. \tag{130}$$

Although both results are based on the same zeroth-order wavefunction, equation (129) is somewhat simpler. In figure 6(*a*), the exchange energy of equation (129) is compared with the exact numerical results of Peek [58]; it is seen that this zeroth-order surface integral result closely follows the exact values over the entire range.

For the H_2 molecule, the zeroth-order home-based wavefunction is of course given by

$$\Phi_0 = \frac{1}{\pi} \exp(-r_{1A}) \exp(-r_{2B}). \tag{131}$$

Using this as Φ_a in equation (127), both the five-dimensional surface integral in the numerator and the six-dimensional volume integral in the denominator can be integrated out analytically [56]. It can be expressed in a closed form:

$$\varepsilon_x = \frac{N}{D}, \tag{132}$$

with

$$\begin{aligned} N = {} & \exp(-2R)\left(\tfrac{1}{30}R^5+\tfrac{1}{30}R^3-R^2-\tfrac{5}{2}\right) \\ & + \mathrm{Ei}(-R)\exp(-R)\left(\tfrac{1}{30}R^6+\tfrac{1}{30}R^5-\tfrac{8}{30}R^4-\tfrac{16}{10}R^3-4R^2-4R\right) \\ & + \mathrm{Ei}(-2R)\left(-\tfrac{4}{10}R^3+4R\right) \end{aligned} \tag{133}$$

and

$$D = 1-\exp(-2R)\left(\tfrac{1}{6}R^3+\tfrac{3}{4}R^2+\tfrac{11}{8}R+1\right), \tag{134}$$

where $\mathrm{Ei}(x)$ is the exponential integral function

$$\mathrm{Ei}(x) = -\int_{-x}^{\infty} \frac{\exp(-t)}{t}\,dt. \tag{135}$$

The exchange energies calculated from the analytical expressions in equations

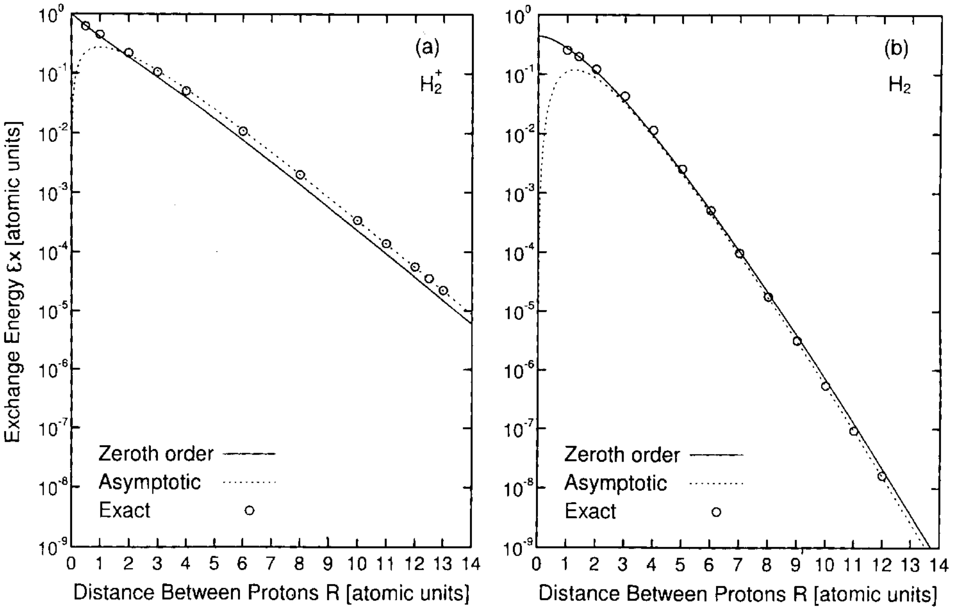

Figure 6. (*a*) Exchange energy of the H_2^+ molecular ion: (——), results obtained from the surface integral method including the denominator with the zeroth-order wavefunction; (· · · · · ·), calculated from the asymptotic exchange energy expression; (○), exact results of Peek [58]. (*b*) Exchange energy of the H_2 molecule: (——), results obtained from the surface integral method including the denominator with the zeroth-order wavefunction: (· · · · · ·), results of the asymptotic exchange energy expression; (○), accurate variational results of Kołos and Wolniewicz [59].

(132)–(134) are shown in figure 6 (*b*) as the solid curve. In the same figure, the 'exact' exchange energies from Kołos and Wolniewicz [59] are shown as open circles for comparison. It is seen that the exchange energy of equation (132) closely follows the exact numerically calculated values in the entire range from 1 to 12 au where they are available.

It is interesting to compare equation (132) with the Heitler–London result which can also be expressed in a closed form [60]. It turns out that, although the expressions are different, they give comparable results from 1 to 12 au [56]. However, there is an important difference. Asymptotically the Heitler–London result goes to [61]

$$\varepsilon_x^{\mathrm{HL}}(R \rightarrow \infty) = \left(\tfrac{28}{45} - \tfrac{2}{15}\gamma - \tfrac{2}{15}\ln R\right) R^3 \exp(-2R), \qquad (136)$$

where γ is the Euler constant equal to 0.5772. As has been noted several times in the past [16, 62], for R larger than $60a_0$, equation (136) becomes negative which is physically unacceptable.

On the other hand, it can be shown that asymptotically the exchange energy of equation (132) is given by [56]

$$\varepsilon_x(R \rightarrow \infty) = \tfrac{4}{15} R^3 \exp(-2R), \qquad (137)$$

which stays positive no matter how large R is. Therefore it does not have the conceptual difficulty of the conventional Heitler–London method.

4.4. *Exact asymptotic exchange energy of H_2^+ and H_2*

As seen in the last section, even the zeroth-order exchange energies closely follow the exact values over the entire range, demonstrating the viability of the surface integral method, but their numerical values are, however, far from 'chemical accuracy'. Based on the surface integral method, one can derive asymptotic expressions which are exact for R going to infinity. The range of validity of these expressions usually includes the well region of the van der Waals potential. Within this range, they are amazingly accurate. Asymptotically, the denominator of both equation (106) and equation (127) can obviously be replaced by unity, and we only need to compute the numerator.

To include the effect of polarization, the localized wavefunction for H_2^+ can be expressed as

$$\Phi_a = \Phi_0\, g(r_a, \theta), \tag{138}$$

where the function g represents the effect of proton B and can be calculated either by the perturbation method [55] or by the Wentzel–Kramers–Brillouin (WKB) approximation [23]. The coordinates r_a and θ are defined in figure 1. The leading term of the exchange energy from the surface integral method with this localized wavefunction is [55]

$$\varepsilon_x = \tfrac{1}{2} R \exp(-R)\, g^2\left(r_a = \frac{R}{2}, \theta = 0\right). \tag{139}$$

To find g, Herring [13] made two approximations which amounts to firstly restricting the equation governing g to the internuclear axis and secondly neglecting the second derivatives of g. These simplifications can be shown to be justified in a calculation of only the asymptotic leading term. Herring found that at $\theta = 0$,

$$g = \frac{1}{1 - r_a/R} \exp\left(-\frac{r_a}{R}\right). \tag{140}$$

Substituting into equation (139), one gets

$$\varepsilon_x(H_2^+, R \to \infty) = \frac{2}{e} R \exp(-R). \tag{141}$$

Herring proved with Kato's [63] theorem that this result is asymptotically exact. For H_2^+, the Schrödinger equation is separable and the asymptotic series of the exchange energy is known [64]. The leading term is indeed given by equation (141). The results of this equation are also shown in figure 6(*a*) as the dotted curve. It is seen that, although this simple expression is exact only asymptotically, it is still amazingly accurate for R as small as 2 au. At the van der Waals minimum (12 au), it is only 1.7% different from the exact value. This is to be compared with the rather complicated second-order SAPT [51] which is in error by 3% at the same distance.

For the H_2 moelcule, Herring and Flicker [16] and Herring [17] used a similar argument and obtained the following expression for the exchange eneregy:

$$\varepsilon_x(H_2, R \to \infty) = 0.818 R^{5/2} \exp(-2R). \tag{142}$$

Although a number of approximations were used to obtain the important effect of electron–electron correlation, Herring [17] was able to show that this expression is asymptotically exact. The results of this equation are also shown in figure 6(*b*) as the dotted curve. Compared with the numerically calculated 'exact' results, this equation is clearly valid in the region of van der Waals minimum (8 au).

It is interesting to note that, when Herring undertook this study, the purpose was to correct the conceptual defect of the Heitler–London method. Even Herring [13] himself thought that this approach is only 'good for the soul'. Later it turned out that equation (142) is in excellent agreement with the most elaborated *ab initio* calculations [59] in the van der Waals region and beyond. This caused some discomfort. For example in their review, Hirschfelder and Meath [6, p. 65] stated, 'Since the unknown correction term $O(R^2 \exp^{-2R})$ might be comparable in magnitude to the first term, the accuracy of the asymptotic values of the exchange energy is not known. The very excellent agreement with the Kołos and Wolniewicz calculations might be fortuitous.' This objection is now removed. Andreev [65] showed that the second term is identically equal to zero. In a recent perturbation calculation [66], the exchange energy was shown to consist of contributions from the zeroth-order wavefunction, ionic distortion and electron–electron correlation. Although they are non-additive, together they give a result identical with equation (142) and the coefficient of the next term $R^2 \exp(-2R)$ is equal to zero. This could be the reason why the leading term alone is such a good approximation, since the best possible result of an asymptotic series is to truncate it at the smallest term.

Another reason why scant attention has been paid to this method in the western literature may be that the surface integral method is based on the physical process of electrons hopping between nuclei. While this phenomenon is in agreement with general principles of physics as beautifully expounded by Feynman [67] and others (for example [68]) and is readily accepted in the case of molecular ions, where the implications from charge-transfer scattering experiments are obvious, it apparently contradicts textbook wisdom. For example, Coulson [69] on p. 113 of the second edition of his famous book *Valence* writes, 'People sometimes say the electrons exchange, or trade places with one another. Such language is full of danger.' Further on the same page, Coulson goes on to state, in connection with the frequency associated with the exchange energy, 'But it is quite incorrect to think of this as an actual frequency of exchange.' Similar statements explicitly warning against this interpretation can be found in many other quantum chemistry textbooks. Of course, one reason for the confusion is that in the conventional approximations the exchange enters in via the exchange integrals, which are not only difficult to give a clear interpretation to, but also give a physically unacceptable asymptotic result [17].

4.5. *Exchange energy of multielectron dimer ions*

The surface integral method for the exchange energy of H_2^+ was extended to multielectron dimer ions by Bardsley *et al.* [23]. It is assumed that the asymptotic exchange energy is due to the outermost electron hopping between the two ionic cores. The localized wavefunction of the outermost valence electron Φ_a is written in the same form as equation (138). Now the zeroth-order wavefunction Φ_0 is the asymptotic wavefunction of the singled-out electron, governed by the equation

$$[-\tfrac{1}{2}\nabla^2 + V(r) + E_I]\,\Phi_0 = 0, \tag{143}$$

where $V(r)$ is the effective potential between the outermost electron and the rest of the particles, and E_I is the atomic ionization energy. In the asymptotic region, the interaction is usually approximated by the Coulomb potential, that is $V(r) = -1/r$. With this potential, the solution can be expressed in terms of the Whittaker function. The radial part is given by [70]

$$\Phi_0 = \frac{1}{(4\pi)^{1/2}} A r^{1/\beta - 1} \exp(-\beta r)\left(1 + \sum_{t=1}^{\infty} \frac{a_t}{r^t}\right), \tag{144}$$

with

$$a_1 = \frac{1}{2\beta}\left[l(l+1) - \frac{1}{\beta}\left(\frac{1}{\beta} - 1\right)\right] \tag{145}$$

and

$$a_t = a_{t-1}\frac{1}{2\beta t}\left[l(l+1) - \left(\frac{1}{\beta} - t\right)\left(\frac{1}{\beta} - t + 1\right)\right], \tag{146}$$

where A is the amplitude, l is the orbital angular momentum of the valence electron and

$$\beta = (2E_I)^{1/2}. \tag{147}$$

For the localized wavefunction Φ_a of equation (138), we must find g which represents the effect of the other ion core. Bardsley *et al.* expressed g in terms of an exponential function $g = \exp(-S_1 - S_2 - \cdots)$ and used the WKB method to find S_1 and S_2 which are successively higher orders of $1/R$. Substituting this Φ_a into the surface integral, they found the exchange energy to be

$$\varepsilon_x = \tfrac{1}{2}\pi R\left(\frac{4}{e}\right)^{1/\beta} \Phi_0^2\left(\frac{R}{2}\right)\left(1 + \frac{C_1}{R} + \frac{C_2}{R^2} + \cdots\right), \tag{148}$$

where C_1 and C_2 are constants depending on β.

If only the leading term in the wavefunction expansion of equation (144) and in the energy expansion of equation (148) are kept, then this last equation is simplified to [71]

$$\varepsilon_{x,1} = \tfrac{1}{2}A^2 R^{2/\beta - 1}\exp\left(-\beta R - \frac{1}{\beta}\right). \tag{149}$$

In the case of H_2^+, for which $\beta = 1$ and $A = 2$, this equation reduces to equation (141), which Herring [13] showed is asymptotically exact. For a general case, his proof should still be valid, provided that the amplitude of the wavefunction A is known exactly.

The exact determination of the amplitude of the asymptotic wavefunction A is in general a difficult problem. A cannot be determined by the normalization condition $(\Phi_0, \Phi_0) = 1$, since the asymptotic wavefunction is not valid at small distances, where the effect of the other electrons cannot be neglected. Thus the most commonly used method to estimate A is to perform a self-consistent field (SCF) calculation for the atomic wavefunction in the inner region and then match it with the asymptotic form at some large distance [71]. While this is a reasonable procedure, it is not without uncertainties. If the matching point is too large, the SCF results are not accurate and, if the matching point is too small, the asymptotic form is no longer valid.

For $l = 0$ electrons a particular simple approximation is to set [70]

$$A = \frac{(2\beta)^{1/\beta}(\beta)^{1/2}}{\Gamma(1/\beta + 1)}. \tag{150}$$

This is commonly known as Bates–Damgaard normalization. It is based on the fact that, if $1/\beta$ is equal to an integer n, the infinite series of equation (144) is broken and becomes a polynomial. In that case, the wavefunction has the same form as a hydrogen orbital. The normalization constants for these orbitals are known analytically:

$$A = \frac{(2/n)^n (1/n)^{1/2}}{\Gamma(n+1)}. \tag{151}$$

When $1/\beta$ is not an integer, the normalization constant is simply interpolated to the form of equation (150). If this normalization is used, then the entire asymptotic exchange energy is determined by the ionization energy alone.

The higher correction terms in the energy expression of equation (148) are known only for H_2^+ with $\beta = 1$ [64]. For arbitrary β, only the first correction term is known [23]:

$$C_1 = \frac{1}{\beta^2}\left(\frac{3}{2\beta} - 1\right). \tag{152}$$

Since the series in equation (148) is an asymptotic series, it is not easy to establish the optimum number of terms to be included. Fortunately often the leading term alone is a very good approximation.

In figure 7, the exchange energies for He_2^+, Li_2^+ and Be_2^+ according to the surface integral method with the normalization of equation (150) are plotted against the internuclear distances [72]. In addition to the leading term $\varepsilon_{x,1}$ of equation (149), the results including additional terms in the wavefunction expansion and in the energy expansion are also shown. $\varepsilon_{x,2}$ denotes the exchange energy calculated with one additional term in the asymptotic wavefunction of equation (144):

$$\varepsilon_{x,2} = \tfrac{1}{2}A^2 R^{2/\beta-1} \exp\left(-\beta R - \frac{1}{\beta}\right)\left(1 + \frac{2p}{R}\right)^2, \tag{153}$$

where

$$p = -\frac{1}{2\beta^2}\left(\frac{1}{\beta} - 1\right). \tag{154}$$

$\varepsilon_{x,3}$ designates the exchange energy for two terms in the wavefunction and two terms in the energy expression (equation (148)):

$$\varepsilon_{x,3} = \tfrac{1}{2}A^2 R^{2/\beta-1} \exp\left(-\beta R - \frac{1}{\beta}\right)\left(1 + \frac{2p}{R}\right)^2\left(1 + \frac{C_1}{R}\right), \tag{155}$$

with C_1 given by equation (152). It is seen that the difference between them is very small.

The general criterion for the validity of the asymptotic energy is [21, 72]

$$R \geqslant \frac{4}{\beta^2}. \tag{156}$$

Therefore we expect the H_2^+, Li_2^+ and Be_2^+ results to be valid for R larger than $2a_0$, $10a_0$ and $6a_0$ respectively.

In figure 7 some 'accurate' *ab initio* results are also shown as open squares. They are obtained from the difference between the energies of *ungerade* and *gerade* states. For He_2^+, they are from the configuration interaction (CI) calculation of Ackermann and Hogreve [73]. These results become unreliable for $R \geqslant 10a_0$. For Li_2^+, they are from the SCF–CI calculation of Schmidt-Mink *et al.* [74], and for Be_2^+ from the

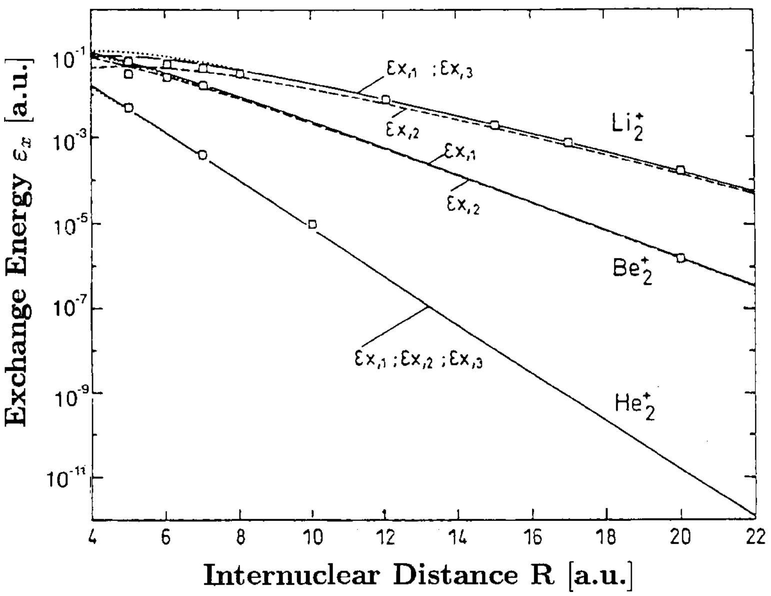

Figure 7. Asymptotic exchange energies of He_2^+, Li_2^+ and Be_2^+. In each case $\varepsilon_{x,1}$, $\varepsilon_{x,2}$ and $\varepsilon_{x,3}$ are shown, they are the one- two- and three-term exchange energy expressions obtained from the surface integral method. The open squares are the 'best' *ab initio* results. For He_2^+ they are from the CI calculation of Ackermann and Hogreve [74], for Li_2^+ from the SCF–CI calculation of Schmidt-Mink *et al.* [74]; and for Be_2^+ from the multireference CI calculation of Fischer *et al.* [75]. (Taken from [72] with permission granted by the American Institute of Physics.)

multireference CI calculation of Fischer *et al.* [75]. It is seen that these *ab inito* results are indeed in very good agreement with the surface integral expressions in the region where they are valid. In fact the simple analytic expressions obtained from the surface integral method with all parameters determined only by the ionization energy are even more accurate than the restricted and unrestricted Hartree–Fock and SCF molecular orbital calculations [72, 76].

It is interesting to note that the difference between the β of Li and He is a factor of only two; yet the exchange energy of Li_2^+ differs from that of He_2^+ by seven orders of magnitude at $R = 20a_0$. The fact that such a simple expression without any adjustable parameters can describe this enormous difference certainly demonstrates the versatility and accuracy of the surface integral method.

4.6. *Exchange energy of multielectron diatomic molecules*

The Gor'kov–Pitaevski and Herring–Flicker method of calculating the asymptotic exchange energy of the H_2 molecule was extented to treat a pair of alkali atoms by Smirnov and Chibisov [18]. In this method, the wavefunction of the valence electron is approximated by the first term of the asymptotic expression in equation (144). In the case of a homonuclear diatomic molecule, the exchange energy is found to be [18]

$$\varepsilon_x = \tfrac{1}{2} D(A, \beta)\, R^{7/2\beta - 1} \exp(-2\beta R), \tag{157}$$

where

$$D(A, \beta) = A^4 \Gamma\left(\frac{1}{2\beta}\right) 2^{-1-1/\beta} \beta^{-2-1/2\beta} \int_0^1 \exp\left(\frac{y-1}{\beta}\right) (1-y)^{3/2\beta} (1+y)^{1/2\beta}\, dy. \tag{158}$$

For $\beta = 1$ and $A = 2$, this equation reduces to the H_2 exchange energy of equation (142). We have found that the β-dependent expression D/A^4 can be fitted to the form [77]

$$\frac{D}{A^4} = 0.0129 + 0.1297\beta - 0.0403\beta^2 \tag{159}$$

with a maximum deviation of only 0.25%. This fit is valid for β varying from 0.5 to 1.4 and equivalent for the ionization energy range from 0.125 to 0.98, which includes all known atoms.

For the heteronuclear interaction, the amplitudes of the wavefunction and the ionization energies for the two atoms will be different. Corresponding to A and β for the first atom, let us define B and α for the second atom. If α and β are not too different, Smirnov and Chibisov [18] showed that the exchange energy calculated by the surface integral method is given by

$$\varepsilon_{\mathrm{x}} = \tfrac{1}{2} R^{2/\alpha + 2/\beta - 1/(\alpha+\beta) - 1} \exp[-(\alpha+\beta)R]\, F(\alpha, \beta, R), \tag{160}$$

where

$$F(\alpha, \beta, R) = A^2 B^2 2^{-2-2/(\alpha+\beta)}\, \Gamma\left(\frac{1}{\alpha+\beta}\right)\left(\frac{2}{\alpha+\beta}\right)^{2+1/(\alpha+\beta)} [H(\alpha, \beta, R) + H(\beta, \alpha, R)] \tag{161}$$

and

$$H(\alpha, \beta, R) = \left(\frac{\alpha+\beta}{2\beta}\right)^{2/\alpha - 2(\alpha+\beta)} \int_0^1 \exp\left(\frac{y-1}{\beta} + R(\beta-\alpha)y\right)(1-y)^{2/\beta - 1/(\alpha+\beta)}$$
$$\times (1+y)^{2/\alpha - 2/\beta + 1/(\alpha+\beta)}\left(1 + \frac{\beta-\alpha}{\beta+\alpha}y\right)^{-2-1/(\alpha+\beta)} \mathrm{d}y. \tag{162}$$

The internuclear distance over which this approximation should be valid is [21]

$$R \geqslant \frac{2}{\alpha^2} + \frac{2}{\beta^2}. \tag{163}$$

The theory was further extended by Duman and Smirnov [20] to treat general atomic systems. It is based on the fundamental approximation that the exchange interaction between two multielectron atoms is dominated by the exchange of a single pair of electrons at any one time. However, in order to antisymmetrize the total wavefunction, the coupling of orbital and spin angular momenta of all equivalent electrons has to be taken into account. As a result, the exchange energy of a multielectron system is found to be equal to the exchange energy of a single pair multiplied by a rather complicated angular momentum coupling constant K, that is

$$\varepsilon_{\mathrm{x}} = K \varepsilon_{\mathrm{x,\,s}}, \tag{164}$$

where $\varepsilon_{\mathrm{x,\,s}}$ is given by equation (157) or (160) and is the exchange energy of a single pair of electrons in the two atoms. To derive the K factor, it is necessary to express the atomic wavefunction in a form in which one valence electron is singled out. This can be done by the genealogical scheme of Racah [78] (see also [79]), in which the atomic wavefunction is written in terms of a single valence electron and of the atomic residue. The total wavefunction of an atom with orbital angular momentum L, spin S and projections M_L and M_S can be expressed as a sum of the products of the wavefunction of the singled-out electron with orbital angular momentum l_1, projection μ and the wavefunction of the atomic residue with orbital angular momentum l and spin s. Since there are several different existing configurations that can be combined with the singled-out valence wavefunction to create the final configuration, each configuration has to be wighted by the fractional parentage coefficient G_{ls}^{LS}. These coefficients are available in tabulated forms [79]. From these atomic wavefunctions, one has to build the molecular wavefunction by combining the two spins S and S' of atom A and atom B to give the total spin J of the molecule. In the asymptotic region, the calculation can be simplified by assuming that only states with $\mu = 0$ will contribute. This is because the main contribution to the exchange energy is from the area close to the internuclear axis [13, 18], where those states with $\mu \neq 0$ have very little density.

The K factor was first calculated by Duman and Smirnov [20] with these approximations. Unfortunately their final results were incorrect. The correct result is given by [80]

$$K = NN'(2S+1)(2S'+1)(2l_1+1)(2l_1'+1)\sum_{sl}\sum_{s'l'}(G_{ls}^{LS})^2 \times (G_{l's'}^{L'S'})^2 \begin{Bmatrix} s & \frac{1}{2} & S \\ \frac{1}{2} & s' & S' \\ S & S' & J \end{Bmatrix} \begin{bmatrix} l & l_1 & L \\ M_L & 0 & M_L \end{bmatrix}^2 \begin{bmatrix} l' & l_1' & L' \\ M_L' & 0 & M_L' \end{bmatrix}^2 \tag{165}$$

where N and N' are the numbers of valence electrons of atom A and atom B respectively. Similarly, all primed quantities are those of atom B. Here $\{\cdots\}$ is the 9-j symbol and $[\cdots]$ is the Clebsch–Gordan coefficient.

The numerical values of the coupling constant K for many diatomic systems have been calculated with equation (165) [80]. Although these K factors are the result of a rather complicated angular momentum coupling, all of them are identical to the results of a simple counting procedure. That is, the factor K is equal to the number of possible exchanges between valence electrons with the same spin in the two atoms. For example, the K values for H–He, He_2, He–Ne and Ar_2 interactions are respectively 1, 2, 6 and 18. Some interaction potentials calculated with these K factors will be discussed in section 5.3. The fact that they differ so greatly from each other and yet in each case an accurate potential is produced is a clear indication that these K factors are correctly predicted. In any case, this counting procedure is consistent with the surface integral method, which associates the exchange energy with only two electrons trading place at any one time.

5. Interaction energy of diatomic systems

5.1. *Exchange energy and polarization approximation*

For some time the surface integral method for the exchange energy was considered to be 'very different in nature from the Rayleigh–Schrödinger perturbation theory involving special analytical techniques which do not appear capable of systematic improvement' [81]. The conventional wisdom was that the exchange terms are 'determined by the region in configuration space where electrons are far away from their parent nuclei; the electronic motion in this region is strongly affected by the non-parent ionic core, which makes a perturbative calculation of these terms unjustifiable' [22]. It now appears that this understanding is not correct as can be seen from the following specific results.

For H_2^+, it can be explicitly shown that the exchange energy receives contributions from all orders of the perturbed wavefunctions, although the dominant contributions are from the first few orders. Replacing the perturbing potential by its multipole expansion [82–84], the exchange energy can be evaluated order by order [55]. Explicitly it can be expressed as

$$\varepsilon_x = \tfrac{1}{2} R \exp(-R) \left(1 + a + \frac{1}{2} a^2 + \frac{1}{3!} a^3 + \cdots + \frac{1}{t!} a^t + \cdots\right)^2, \tag{166}$$

where

$$a = \sum_{n=1}^{\infty} \frac{1}{n+1} \left(\frac{1}{2}\right)^{n+1}. \tag{167}$$

The first term in equation (166) is from the zeroth-order wavefunction, the second term from the first-order wavefunction, and so on. Equation (166) can be written as

$$\varepsilon_x = \tfrac{1}{2} R \exp(-R) (\exp a)^2 \tag{168}$$

and, since

$$\sum_{n=1}^{\infty} \frac{1}{n+1} \left(\frac{1}{2}\right)^{n+1} = \ln 2 - \tfrac{1}{2}, \tag{169}$$

hence

$$\begin{aligned} \varepsilon_x &= \tfrac{1}{2} R \exp(-R) [\exp(\ln 2 - \tfrac{1}{2})]^2 \\ &= \frac{2}{e} R \exp(-R), \end{aligned} \tag{170}$$

which is the exact asymptotic exchange energy of equation (141). The coefficient of $R \exp(-R)$ is an irrational number. It is interesting to see that the perturbation series actually converges to this irrational number exactly. Although it takes infinite orders to arrive at this irrational number, in practice the rate of convergence is rather fast. The zeroth-order wavefunction gives 67.95% of the exact value. Together with the first-order wavefunction (two terms in equation (166)), it is already 96.74%. With second order, 99.79%. With the first four orders of the wavefunctions, essentially 100% of the exchange energy is recovered.

These explicit analytical results conclusively demonstrate that the exchange energy can be calculated perturbatively and that the exact asymptotic exchange energy contains the polarization effects.

5.2. *Generalized Heitler–London theory and potential of the chemical bond*

For H_2^+, with Φ_0 given by the 1s orbital, ε_1 and s_0 are well known [31]:

$$\varepsilon_1 = \left(1 + \frac{1}{R}\right) \exp(-2R), \tag{171}$$

$$s_0 = \left(1 + R + \frac{R^2}{3}\right) \exp(-R). \tag{172}$$

The exchange energy ε_x calculated by the surface integral method is given by equation (129). Substituting them into equation (61) with $M = 1$, we obtain the $\Sigma_g\, H_2^+$ ground-state potential $(E_s - \varepsilon_0)$ shown as the dashed curve in figure 8.

For this system, Dalgarno and Lynn [85] obtained the exact first-order wavefunction Φ_1 by solving equation (36) in confocal elliptical coordinates. With this exact

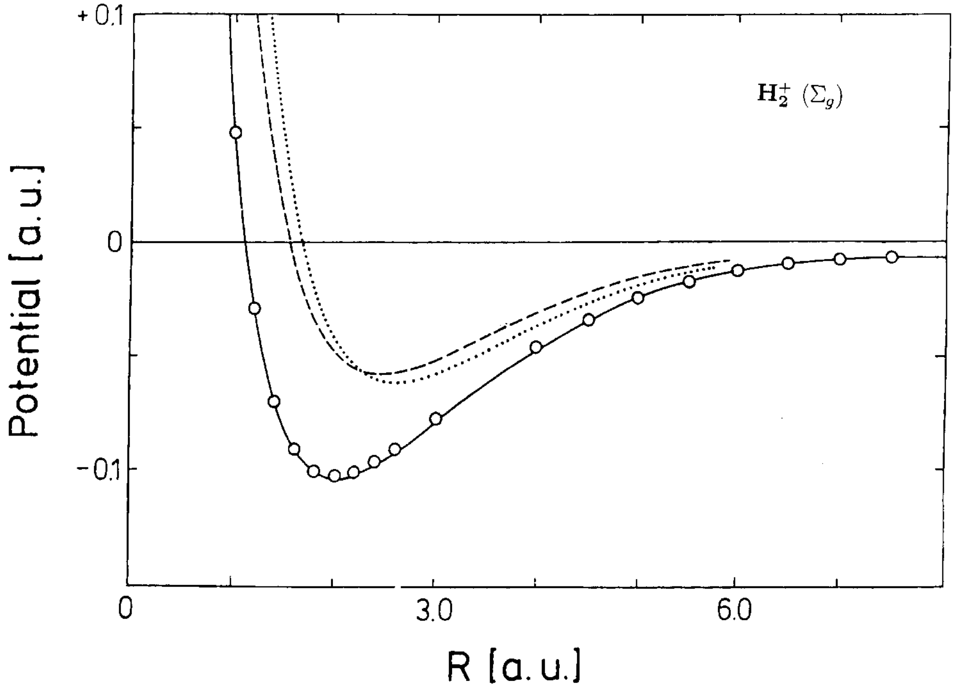

Figure 8. Ground-state potential energy of the H_2^+ molecular ion calculated by the GHL theory with polarization wavefunctions: (– – –), calculated with the zeroth-order wavefunction; (——), calculated with the exact zeroth- and first-order polarization wavefunctions; (○), exact results from Peek [58]; (· · · · · ·), for comparison, the usual Heitler–London (linear combination of atomic orbitals) energy with the zeroth-order symmetrized wavefunction. (Taken from [57] with permission granted by the American Institute of Physics).

first-order wavefunction, Chipman and Hirschfelder [53] evaluated analytically the first-order overlap s_1 and the second-order polarization energy ε_2. Approximating the localized wavefunction $\Phi_a = \Phi_0 + \Phi_1$, the exchange energy of equation (106) was evaluated in closed forms by Guo *et al.* [86]. Therefore the potential from equation (61) with $M = 2$ can also be expressed in terms of analytic functions [57]. This potential is shown in figure 8 as the solid curve. In the same figure, the exact results from Peek [58] are also shown as open circles. The amazing agreement shown in the figure clearly demonstrates that through the GHL theory the chemical potential can be calculated perturbatively and the results are drastically improved by going from zeroth-order to first-order wavefunctions.

The GHL theory has also been implemented for the calculation of the ground state (X $^1\Sigma_g^+$) potential of the H_2 molecule [87]. Since closed expressions are not available, up to 240 variational terms are used for various orders of perturbed wavefunctions. Polarization energies ε_n and overlap integrals s up to $n = 60$ have been numerically evaluated. Rapid convergence of the GHL equation (equation (61)) is achieved for all distances if an accurate exchange energy is used. This result is quite important since, although previous attempts to use perturbation theory to calculate the potential of the chemical bond have not been successful, it has long been known that the exchange energy can be calculated accurately. For example, already in 1968 Certain *et al.* [88] reported on the basis of an examination of various perturbation methods that equally good results for the exchange energy could be obtained from different methods. Recently we have demonstrated [89] that, by using the well known Coulson-Fischer [90] orbital, the error in the exchange energy obtained from the surface integral method is reduced from 20% in the zeroth-order wavefunction calculation to only 4% in the region of chemical bonds. Thus, in view of these results, the less accurate interaction energies obtained by Certain *et al.* [88] can be greatly improved by the use of equation (61).

While other chemical bond potentials have been determined by the GHL theory [91], it is for the calculation of van der Waals potentials that the GHL theory (equation (62)) is especially useful.

5.3. *Generalized Heitler–London theory and van der Waals potential*

Standard computational methods of electronic structure theory are not well suited to the determination of the weak van der Waals potentials [92]. Essentially the difficulties arise from the errors inherent in the subtraction of the enormous energies of the separated atoms from that of the combined supermolecule which are only slightly different. Therefore many attempts have been made throughout the years to construct a composite semiempirical potential by adding the repulsive and attractive parts [93–104]. It is well known that the long-range attractive potential can be described by the dispersion series obtained from the second-order perturbation theory [7]. As we have discussed, the repulsion is mainly due to the exchange effect. Later it became clear that a large part of this repulsion can be obtained from a molecular SCF calculation [93]. Thus the SCF results are used for the repulsive parts in many of these potential models. The problem of divergence of the dispersion series at small R is solved in the Tang–Toennies [9] potential model by a simple damping function which gradually turns off each individual term. These damping functions were derived from a classical Drude model and depend only on the range parameter of the repulsive potential. Thus they can be applied to all systems. For systems for which accurate *ab initio* damping functions are available [105, 106], they are found to be very accurate. However, for this model to give correct absolute values of the potentials for both atom–atom [9] and atom–molecule [107, 108] interactions, it was found necessary to increase the SCF results by 14–17%. It can be argued that this increase is required to account for the exchange–dispersion. In principle this term can be recovered from the SAPTs, but in practice it is extremely difficult to calculate directly [109–111].

While useful for understanding a variety of experimental data, this simple potential model has two problems: firstly the *ad hoc* nature of adding together the repulsive and attractive parts from different sources, and secondly the necessity of estimating the exchange–dispersion energy.

With the GHL theory, these problems are solved. The van der Waals potential is given by equation (62) which is derived from a single consistent theory. The exchange energy calculated by the surface integral method automatically contains the dispersion (polarization) effects, as we have seen in section 5.1. In this theory, the polarization energy and the exchange energy are combined in a computationally and conceptually simple way. If the region of validity for the asymptotic energy covers the well region of the vander Waals potential, often an accurate analytic potential can be obtained.

The $^3\Sigma_u$ state potential of the H_2 molecule is an important prototype of the van der Waals potentials [99]. The potential energy, defined as $V = E_t - \varepsilon_0$, is given by equation (62). With $M = 2$,

$$V = \varepsilon_1 + \varepsilon_2 + (1 + s_0 + s_1)\,\varepsilon_x. \qquad (173)$$

The first-order energy ε_1 and zeroth-order overlap are well known [31]:

$$\varepsilon_1 = \left(\frac{1}{R} + \tfrac{5}{8} - \tfrac{3}{4}R - \tfrac{1}{6}R^2\right) \exp(-2R), \tag{174}$$

$$s_0 = (1 + R + \tfrac{1}{3}R^2)^2 \exp(-2R). \tag{175}$$

The first-order overlap s_1 is negligibly small in the van der Waals region [87]. The accurate second order polarization energy ε_2 is also available [8] and can be expressed in terms of the dispersion series

$$\varepsilon_2 = -\sum_{n=3} f_{2n}(R)\, C_{2n}\, R^{-2n}, \tag{176}$$

where the C_{2n} are the dispersion coefficients and the f_{2n} are the damping functions. For the hydrogen molecule, the dispersion coefficients are known exactly. Using the Tang–Toennies [9, 112] damping functions

$$f_{2n} = 1 - \exp(-bR) \sum_{k=0}^{2n} \frac{(bR)^k}{k!}, \tag{177}$$

with

$$b = -\frac{\mathrm{d}}{\mathrm{d}R} \ln[\varepsilon_{\mathrm{x}}(R)] \tag{178}$$

and the exchange energy ε_{x} of equation (142), the potential of equation (173) can be evaluated analytically. The results are shown in figure 9. For comparison, the numerically calculated 'exact' results of Kołos and Wolniewicz [59] are also shown in the same figure as open circles. For $R \geqslant 3$ au, they are hardly distinguishable. At the well minimum (8 au) they differ from each other by only 0.5% [113].

Recently equation (173) was used to calculate the potentials of He_2, Ne_2 and Ar_2 [114]. The exchange energy was calculated from equation (164) with $\varepsilon_{\mathrm{x,\,s}}$ given by equation (157) and K given by the counting rule. The amplitude A of the wavefunction was determined from a comparison with the atomic density obtained from a configuration interaction calculation. The first-order energy, which is the Coulomb integral, was evaluated with the asymptotic wavefunction. The overlaps were also numerically evaluated and found to be negligibly small in the well region. The second-order energy was calculated using equation (176). For these systems, the first three dispersion coefficients are accurately known [115] and the higher coefficients are estimated through the recurrence relation [116, 117]

$$C_{2n} = \left(\frac{C_{2n-2}}{C_{2n-4}}\right)^3 C_{2n-6}. \tag{179}$$

Again the Tang–Toennies damping functions of equation (178) were used. Recently Wheatley and Meath [118] did an elaborate calculation for the damping function of the He_2 potential. Their results are found to be in very good agreement with equation (177) in the well region [114].

The potentials of He_2 and Ar_2 obtained from equation (173) are shown in figures 10(*a*) and 10(*b*) respectively [114]. For He_2, the results of the quantum Monte Carlo calculation of Anderson *et al.* [119] and the multireference CI calculation of van Mourik and van Lenthe [120] are also shown for comparison. For this system the input parameters to the GHL theory are accurately known; the results are almost of

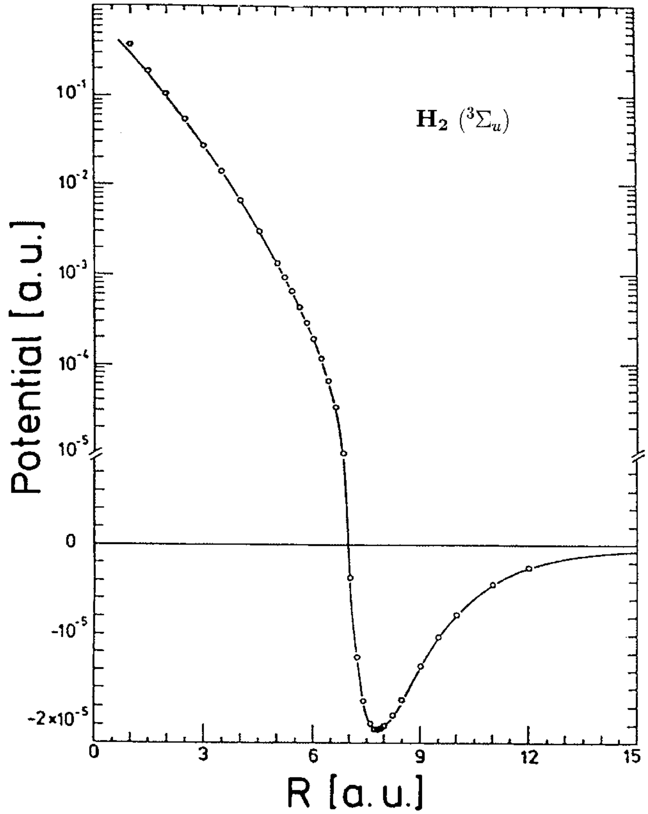

Figure 9. The van der Waals potential $V(R)$ of the $H_2(^3\Sigma_u)$ system : (——), results of the GHL theory with the asymptotic exchange energy; (○), numerical *ab initio* 'exact' results of Kołos and Wolniewicz [59]. (Taken from [113] with permission granted by Springer–Verlag.)

spectroscopic precision. For Ar_2, the results of the fourth-order Møller–Plesset calculation of Tao and Pan [121] as well as the empirical fit of Aziz and Slaman [122] are also shown. While the GHL results are comparable with the 'best' *ab initio* calculations now available, an error of up to 10% cannot be ruled out. Most of this error comes from the uncertainty in the asymptotic amplitude A of the atomic wavefunction. Although how to precisely determine the value A is an interesting problem for further investigation, the advantage of the surface integral method is clear. It has transformed the two-centre molecular problem to a one-centre atomic problem which should be much simpler to handle. It is interesting to note that according to the counting rule, K is equal to 2 for He_2 and to 18 for Ar_2. In the original paper of Duman and Smirnov [20], it is equal to 9 for both cases. If the value of 9 is used, the potentials produced are nowhere near those shown in figure 10.

In these calculations it is found that the first-order energy contributes less than 10% to the well minimum and, to a good approximation, is proportional to the exchange energy. It also happens that the value of A determined from an accurate CI atomic wavefunction is larger than that obtained from the SCF wavefunction by about 2–3%. Since the exchange energy depends on the fourth power of A, this just about cancels the first-order energy. Therefore, for simplicity, one can use the A value determined by the atomic SCF calculation and neglect the first-order energy. For a

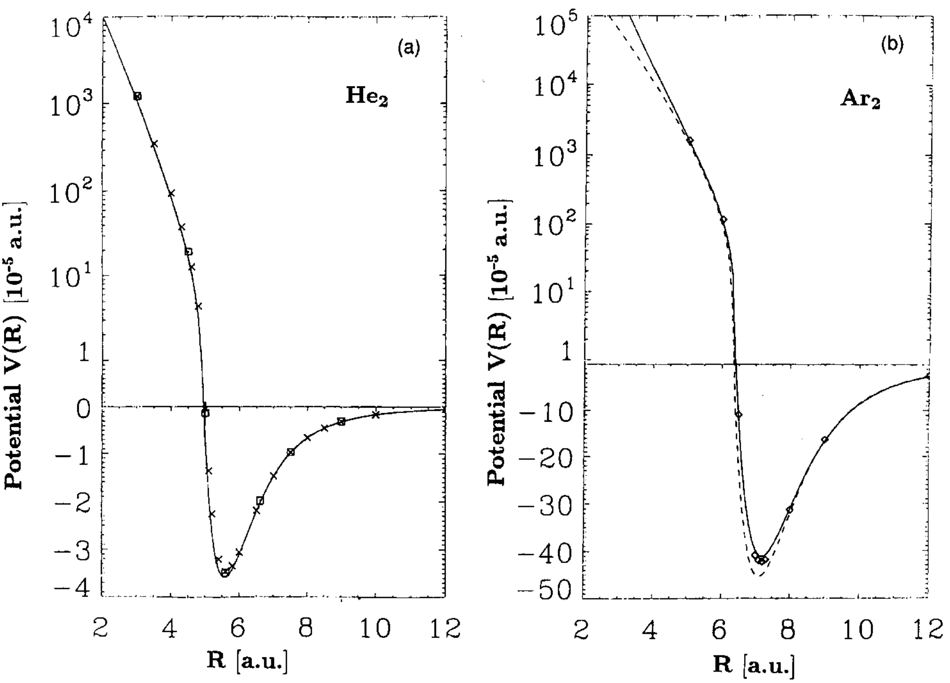

Figure 10. (*a*) The He_2 potential curve: (——), results of the GHL theory with the asymptotic exchange energy; (□), the quantum Monte Carlo calculations of Anderson *et al.* [119]; (×), the multireference CI calculation of van Mourik and van Lenthe [120]. (*b*) The Ar_2 potential curve: (——), results of the GHL theory with the asymptotic exchange energy; (◇), fourth-order Møller–Plesset calculation of Tao and Pan [121]; (– – –), empirical multiproperty fit of Aziz and Slaman [122]. (Taken from [114] with permission granted by the American Institute of Physics.)

homonuclear dimer, the entire van der Waals potential is thus given by the closed analytical expression

$$V = \tfrac{1}{2} K D R^{7/2\beta - 1} \exp(-2\beta R) - \sum_{n=3} \left(1 - \exp(-bR) \sum_{k=0}^{2n} \frac{(bR)^k}{k!} \right) \frac{C_{2n}}{R^{2n}} \tag{180}$$

with

$$b = 2\beta - \frac{3.5\beta - 1}{R}. \tag{181}$$

Results based on this model differs very little from what is shown in figure 10 [114, 123].

For heteronuclear systems, the exchange energy of a single pair of electrons should be calculated with equation (160). We have used this equation to calculate the van der Waals potentials of H–He, He–Ne, Li–He, Na–He, K–He, Rb–He and Cs–He [77]. In every case, the agreement with the best *ab initio* data or semiempirical potentials is very good. Equation (160) is strictly valid for $\alpha \approx \beta$. However, even for interactions, such as Li–He ($\alpha = 0.629$; $\beta = 1.344$), where the difference between them is a factor of two, the formula apparently still works. The true range of validity of these formulae is another interesting problem for further investigation.

6. Interaction energy of the H_3 system

6.1. *Complete H_3 potential energy surfaces according to the generalized Heitler–London theory*

In the case of H_3, the symmetry group is S_3 which has six elements. This group has three irreducible representations which we shall designate as A, B and E. Both A and B are one dimensional, and E is two dimensional. The matrix representing each of the elements have the following explicit forms [45]:

$$D^A(g) = 1 \text{ for all } g \text{ in } S_3, \tag{182}$$

$$D^B(g) = 1 \text{ for } g = I, (123), (132), \tag{183}$$

$$D^B(g) = - 1 \text{ for } g = (12), (23), (13). \tag{184}$$

$$D^E(I) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \tag{185}$$

$$D^E(12) = \frac{1}{2}\begin{pmatrix} -1 & 3^{1/2} \\ 3^{1/2} & 1 \end{pmatrix}, \tag{186}$$

$$D^E(23) = \frac{1}{2}\begin{pmatrix} -1 & -3^{1/2} \\ -3^{1/2} & 1 \end{pmatrix}, \tag{187}$$

$$D^E(13) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{188}$$

$$D^E(123) = \frac{1}{2}\begin{pmatrix} -1 & 3^{1/2} \\ -3^{1/2} & -1 \end{pmatrix}, \tag{189}$$

$$D^E(132) = \frac{1}{2}\begin{pmatrix} -1 & -3^{1/2} \\ 3^{1/2} & -1 \end{pmatrix}. \tag{190}$$

With $n_A = n_B = 1$ and $n_E = 2$, and the order of the group N equal to 6, the projection operators can be directly calculated by putting these explicit representations into equation (20). In particular,

$$P_{11}^A = \tfrac{1}{6}[I + (12) + (23) + (13) + (123) + (132)], \tag{191}$$

$$P_{11}^B = \tfrac{1}{6}[I - (12) - (23) - (13) + (123) + (132)]. \tag{192}$$

Since both representations A and B are one dimensional, the eigenfunctions belonging to thse representations are basis functions. These eigenfunctions can be projected out from a single localized wavefunction shown in equation (21). Then it is clear from equation (191) that the eigenfunction u^A of representation A is totally symmetric with respect to its spatial coordinates. To satisfy the Pauli principle, the spin function is required to be antisymmetric, which is not possible with three electrons. Therefore this is an unphysical state. We designate the eigenvalue of this 'mathematical' state E':

$$E' = H_{11}^A. \tag{193}$$

Similarly, since P_{11}^B of equation (192) is antisymmetric in the exchange of two electrons, the eigenfunction u^B must be also antisymmetric in spatial coordinates. Accordingly its spin function must be symmetric. Therefore this is the spin-$\frac{3}{2}$ state, and we designate its eigenenergy $E_{3/2}$ as

$$E_{3/2} = H_{11}^B. \tag{194}$$

The representation E is two dimensional; the basis functions can be formed by linear combinations of the eigenfunctions belonging to this representation. The eigenvalues are doubly generate and can be obtained from diagonalizing the Hamiltonian matrix with respect to the basis functions [124, 125]. These wavefunctions are associated with the doublet spin-$\frac{1}{2}$ states [126], and we designate the corresponding eigenenergies $E_{\pm}$.

Putting the representations of equations (182)–(190) into equation (30), we obtain the following matrix elements of the Hamiltonian:

$$H_{11}^{A} = \varepsilon_I + \varepsilon_{12} + \varepsilon_{13} + \varepsilon_{23} + \varepsilon_{123} + \varepsilon_{132}, \tag{195}$$

$$H_{11}^{B} = \varepsilon_I - \varepsilon_{12} - \varepsilon_{13} - \varepsilon_{23} + \varepsilon_{123} + \varepsilon_{132}, \tag{196}$$

$$H_{11}^{E} = \varepsilon_I - \tfrac{1}{2}\varepsilon_{12} + \varepsilon_{13} - \tfrac{1}{2}\varepsilon_{23} - \tfrac{1}{2}\varepsilon_{123} - \tfrac{1}{2}\varepsilon_{132}, \tag{197}$$

$$H_{22}^{E} = \varepsilon_I + \tfrac{1}{2}\varepsilon_{12} - \varepsilon_{13} + \tfrac{1}{2}\varepsilon_{23} - \tfrac{1}{2}\varepsilon_{123} - \tfrac{1}{2}\varepsilon_{132}, \tag{198}$$

$$H_{12}^{E} = \frac{3^{1/2}}{2}(\varepsilon_{12} - \varepsilon_{23} - \varepsilon_{123} + \varepsilon_{132}), \tag{199}$$

$$H_{21}^{E} = \frac{3^{1/2}}{2}(\varepsilon_{12} - \varepsilon_{23} + \varepsilon_{123} + \varepsilon_{132}). \tag{200}$$

Because of the Wigner theorem in equation (23), the matrix of the Hamiltonian with respect to the basis $\{u_{11}^{E}, u_{12}^{E}, u_{21}^{E}, u_{22}^{E}\}$ is of the form

$$\begin{bmatrix} H_{11}^{E} & H_{12}^{E} & 0 & 0 \\ H_{21}^{E} & H_{22}^{E} & 0 & 0 \\ 0 & 0 & H_{11}^{E} & H_{12}^{E} \\ 0 & 0 & H_{21}^{E} & H_{22}^{E} \end{bmatrix}. \tag{201}$$

By diagonalizing this matrix, the degenerate eigenenergies are found to be

$$E_{\pm} = \tfrac{1}{2}\{H_{11}^{E} + H_{22}^{E} \pm [(H_{11}^{E} - H_{22}^{E})^2 + 4H_{12}^{E}H_{21}^{E}]^{1/2}\}. \tag{202}$$

With equations (197)–(200), this equation becomes

$$E_{\pm} = \varepsilon_I - \varepsilon_{123} \pm \{\tfrac{1}{2}[(\varepsilon_{12} - \varepsilon_{23})^2 + (\varepsilon_{23} - \varepsilon_{31})^2 + (\varepsilon_{31} - \varepsilon_{12})^2]\}^{1/2}, \tag{203}$$

where we have used the identity $\varepsilon_{123} = \varepsilon_{132}$.

Substituting ε_I from equation (44) into equation (203), we obtain

$$E_{\pm} = \sum_{n=0} \varepsilon_n - \sum_{g \neq I} \sum_{n=0} \varepsilon_g \langle \Phi_0, T(g)\, \Phi_n \rangle - \varepsilon_{123} \pm \{\tfrac{1}{2}[(\varepsilon_{12} - \varepsilon_{23})^2 + (\varepsilon_{23} - \varepsilon_{31})^2 + (\varepsilon_{31} - \varepsilon_{12})^2]\}^{1/2}. \tag{204}$$

It should be recalled that ε_n is the nth-order polarization energy calculated from the unsymmetrized Rayleigh–Schrödinger perturbation theory. Since Φ_0 is the product of three hydrogenic atomic orbitals, ε_0 is simply the sum of the energies of the three isolated hydrogen atoms. Therefore the two lowest sheets of the H_3 potential energy surfaces are

$$V_{\pm} = E_{\pm} - \varepsilon_0. \tag{205}$$

The first-order polarization energy is simply the sum of the three Coulomb integrals. The polarization energy of the three-body system consists of the sum of all orders of the two-body terms which are obtained without considering the presence of the third atom, and the non-additive three-body terms which do not show up until third order (for example [127]). The well known Axilrod–Teller–Muto [128] triple dipole interaction is the leading term in the non-additive three-body interaction in the asymptotic region. Similarly, $\langle \Phi_0, T(g)\, \Phi_n \rangle$ can also be separated into two-body and three-body overlap integrals. The exchange energy ε_g, although formally defined by equation (29), reduces to ε_{12} of equation (53) when the third atom is far away. Therefore, if g involves an interchange of only two indices, then ε_{ij} can be expressed as the exchange energy of a diatomic system plus terms involving the effect of the presence of the third atom [46].

6.2. *Generalized Heitler–London theory and semiempirical potential energy surfaces*

Because of its completeness, equation (204) provides a benchmark theory, which will be used here to assess several previous approximate theories.

6.2.1. *The London formula*

Neglecting in equation (204) firstly all overlap integrals, secondly all orders of polarization energy ε_n for $n > 1$, and thirdly all three-body effects, we obtain the doublet potential energy surfaces $V_\pm$ from equation (205):

$$V_\pm = \varepsilon_1(R_1) + \varepsilon_1(R_2) + \varepsilon_1(R_3) \pm \frac{1}{2^{1/2}} \times \{[\varepsilon_{\mathrm{x}}(R_1) - \varepsilon_{\mathrm{x}}(R_2)]^2 + [\varepsilon_{\mathrm{x}}(R_2) - \varepsilon_{\mathrm{x}}(R_3)]^2 + [\varepsilon_{\mathrm{x}}(R_2) - \varepsilon_{\mathrm{x}}(R_3)]^2\}^{1/2}, \tag{206}$$

where R_1, R_2 and R_3 are the three internuclear distances. Since without overlap the first order polarization energy ε_1 is the Coulomb integral and the exchange energy ε_{x} is the exchange integral, equation (206) is the equation which London [129] reported in 1929 without proof and for which a derivation was later provided by Kassel [130] in 1932.

6.2.2. *The Slater formula*

Neglecting in equation (204) firstly all overlap integrals, secondly all orders of polarization energy ε_n for $n > 1$, and thirdly all three-body effects except the exchange energy ε_{123} coming from the cyclic permutation of electrons, the doublet potential energy surfaces $V_\pm$ become

$$V_\pm = \varepsilon_1(R_1) + \varepsilon_1(R_2) + \varepsilon_1(R_3) - \varepsilon_{123} \pm \frac{1}{2^{1/2}} \times \{[\varepsilon_{\mathrm{x}}(R_1) - \varepsilon_{\mathrm{x}}(R_2)]^2 + [\varepsilon_{\mathrm{x}}(R_2) - \varepsilon_{\mathrm{x}}(R_3)]^2 + [\varepsilon_{\mathrm{x}}(R_3) - \varepsilon_{\mathrm{x}}(R_1)]^2\}^{1/2}. \tag{207}$$

Again identifying ε_1 and ε_{x} as respectively the Coulomb integral and the exchange integral because the overlap integral is neglected, this is the equation that Slater [131] derived in 1931 with a different approach.

6.2.3. *The valence bond theory*

An approximate expression comparable with the valence bond formula is obtained from equation (204) by neglecting firstly all overlap integrals except s_0, secondly all orders of polarization energy ε_n for $n > 1$, and thirdly all three-body effects

$$V_\pm = \sum_{i=1}^{3} [\varepsilon_1(R_i) + s_0(R_i)\, \varepsilon_{\mathrm{x}}(R_i)] \pm \frac{1}{2^{1/2}} \times \{[\varepsilon_{\mathrm{x}}(R_1) - \varepsilon_{\mathrm{x}}(R_2)]^2 + [\varepsilon_{\mathrm{x}}(R_2) - \varepsilon_{\mathrm{x}}(R_3)]^2 + [\varepsilon_{\mathrm{x}}(R_3) - \varepsilon_{\mathrm{x}}(R_1)]^2\}^{1/2}. \tag{208}$$

Here ε_1 and s_0 are identical with the two-body Coulomb integral and the overlap integral respectively of the H_2 system. This equation should contain the same amount of information as the valence bond theory. Note that, in equation (208), ε_{x} is the exchange energy of equation (12) instead of the exchange integral usually used in valence bond theory. The complete valence bond expression in which the overlap is not neglected has been derived by Slater [131] and by Eyring and Lin [132]. It looks far more complicated than equation (208). The difference in the appearance arises because, if the overlap is not neglected, the exchange energy is not the same as the exchange integral. This difference has already shown up in the H_2 system. Expressed in terms of exchange integrals, the H_2 Heitler–London energies are given by equations (6) and (7) where the overlap integral appears inside a polynomial in the denominator. Expressed in terms of the exchange energy, the same set of Heitler–London energies is given by equations (14) and (15) where there is no denominator and the overlap integral appears in combination with the exchange energy as an additive term. In the present formulation of the H_3 potential surfaces the overlap integrals also appear as additive terms as seen in equation (208). The complications in the usual valence bond H_3 formulation is due to the necessity of combining many terms with polynomials in the denominator. When one atom is far away, the valence bond expression will reduce directly to equations (6) and (7), whereas the present formulation of equation (208) will reduce to equations (14) and (15). As we have shown, they are completely equivalent.

6.2.4. *Semiempirical potential surfaces*

The celebrated LEPS potential energy surface is based on the valence bond theory. Eyring and Polanyi [133] implemented the London [129] formula with an approximate exchange integral. Sato [134] suggested the use of a denominator to simulate the overlap integrals in the valence bond theory. The LEPS equation has had a tremendous impact on chemical dynamics and a large amount of work has been devoted to the improvements of this semiempirical potential surface. One of the best known is the Porter–Karplus [135] surface. They used the complete valence bond equation including the Coulomb, the exchange and the overlap integrals. They also tried to include some three-body effects in the exchange integral. This effect is different from the cyclic exchange ε_{123} in the Slater formula. It comes from the fact that the three electronic coordinates in the Hamiltonian sandwiched in the exchange integral are scrambled, even though only two electrons are interchanged in the wavefunction. In their original version, they introduced some empirical parameters and produced a reasonably accurate potential surface. However, when the more accurate triplet H_2 energies, which became available afterwards, were used in their formula, it actually gives a rather poor surface (for example [136]).

6.2.5. *The Cashion–Herschbach formula*

Neglecting in equation (204) all three-body effects, but including all orders of two-body terms, we obtain

$$E_{\pm} = \sum_{i=1}^{3}\left(\sum_{n=0}[\varepsilon_n(R_i) + \varepsilon_{\mathrm{x}}(R_i)\, s_n(R_i)]\right) \pm \frac{1}{2^{1/2}}$$
$$\times\{[\varepsilon_{\mathrm{x}}(R_1) - \varepsilon_{\mathrm{x}}(R_2)]^2 + [\varepsilon_{\mathrm{x}}(R_2) - \varepsilon_{\mathrm{x}}(R_3)]^2 + [\varepsilon_{\mathrm{x}}(R_3) - \varepsilon_{\mathrm{x}}(R_1)]^2\}^{1/2}. \quad (209)$$

Using equation (58), we can write this equation as

$$E_{\pm} = \varepsilon_{\mathrm{C}}(R_1) + \varepsilon_{\mathrm{C}}(R_2) + \varepsilon_{\mathrm{C}}(R_3) \pm \frac{1}{2^{1/2}}$$
$$\times\{[\varepsilon_{\mathrm{x}}(R_1) - \varepsilon_{\mathrm{x}}(R_2)]^2 + [\varepsilon_{\mathrm{x}}(R_2) - \varepsilon_{\mathrm{x}}(R_3)]^2 + [\varepsilon_{\mathrm{x}}(R_3) - \varepsilon_{\mathrm{x}}(R_1)]^2\}^{1/2}. \quad (210)$$

Cashion and Herschbach [40] obtained this equation semiempirically. First they neglected the overlap integrals in the valence bond theory; so they started out with the London formula. Then they neglected the overlap integrals again in the Heitler–London energies of the H_2 molecule. They replaced the Coulomb integral and the exchange integral by half the sum and difference of the triplet and singlet state energies of the H_2 molecule. As seen in the present development, in so doing they have unknowingly included not only the overlap integrals, which they thought were neglected, but also all orders of the two-body terms. This is because in reality they have used the Coulomb energy and the exchange energy which contain all orders of the two-body interactions. Therefore, if the accurate energies of the H_2 molecules are used, this potential surface should be superior to other semiempirical surfaces based on the valence bond theory, in which only the first-order Coulomb, the exchange and the overlap integrals are used.

6.2.6. *Diatomic-in-molecule surface*

It is interesting to note that the diatomic-in-molecule (DIM) potential energy surface [137] without overlap is also identical with equation (210) [138]. There are two versions of DIM surfaces: one with and the other without overlap. Because of the way that the Hamiltonian is divided and regrouped, the term ‘overlap’ in DIM is used in a somewhat different context. Experience is that the version without overlap works better. It is also this version that is identical with equation (210). According to the present theory, equation (210) already contains all two-body overlaps. The extra overlap in the other version comes from the implicit assumption of the DIM method. It is equivalent to regarding ε_C and ε_X in equation (210) as the Coulomb integral and the exchange integral respectively and then to add overlap integrals to the equation. This results in double counting.

Since accurate triplet and singlet state energies of the H_2 molecule are now available, equation (210) is a parameter-free potential surface. Not only does this surface give a fairly accurate potential in the saddle-point region [40, 137], but even in the H_2–H van der Waals region it is not too far from the *ab initio* surface [139]. This is to be contrasted with other semiempirical surfaces. For example, the Porter–Karplus potential surface does not give a well in the van der Waals region [140]. Whereas other semiempirical surfaces include only first-order quantities, equation (210) includes all orders of two-body interactions. This explains why it correctly predicts the van der Waals attraction which is contained in the second-order polarization energy.

While equation (210) may be sufficient for a qualitative understanding, to achieve ‘chemical accuracy’ it is still necessary to include the three-body effects. The GHL theory enables us to calculate these effects systematically. For example, the ε_{123} exchange energy due to cyclic permutation of the three electrons can also be calculated by the surface integral method [24, 141]. When this term is added to equation (210), the potential surface for nonlinear configurations is substantially improved [142].

7. Concluding remarks

In this paper we have shown that the complexity of the problem of symmetry in calculating the interatomic potentials can be reduced to its simplest level by the irreducible representations of the permutation group, to which the total Hamiltonian belongs. The eigenenergies of the Hamiltonian are calculated from a set of basis functions of these representations which are projected out from a localized wavefunction obtained from the Schrödinger equation with the unsymmetrized perturbation theory. When these eigenenergies are expanded in terms of exchange integrals order by order, almost all previous SAPTs for diatomic systems are shown to be subsets of these expansions. Since the lowest order is identical with the usual Heitler–London energy, we call this theory the GHL theory. The advantage of this theory is that, instead of exchange integrals, the exchange energy obtained from the surface integral method can be used directly. According to the GHL theory, the van der Waals potentials depend only on the known dispersion coefficients, the amplitude of the asymptotic wavefunctions, and the ionization energies of the individual atoms. With these atomic parameters, potential curves with well minimum ranging from 0.4×10^{-5} (Cs–He) to 40×10^{-5} (Ar_2) are predicted with a simple expression to a high degree of accuracy. This strongly suggests that the essential physics of the interaction are included in the GHL theory and the surface integral method is an efficient way to calculate the exchange repulsion.

The GHL theory can also be used to find a systematic way to study triatomic potential energy surfaces. The GHL theory of the H_3 potential surface, just like its counterpart for diatomic systems, is very useful in summarizing previous theories and pointing the direction for further improvement. In this way we have gained direct insight into the basic structure of the H_3 potential energy terms. Clearly the S_n permutation group can be applied equally well to H_n systems. A calculation of the energy surface of H_4 using the method described here is at present in progress [142]. We envisage that ultimately a more clear picture of the potentials of small open-shell clusters will emerge through this line of investigation.

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