ON THE SYMMETRY AND MOLECULAR DYNAMICAL ORIGIN OF MAGNETO CHIRAL DICHROISM: "SPIN CHIRAL DICHROISM" IN ABSOLUTE ASYMMETRIC SYNTHESIS

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It is shown that a chiral influence, consisting of a combination of fields, is accompanied in the laboratory frame (X, Y, Z) by nine elements of the time cross correlation function $\langle v(t)\,\omega^{T}(0)\rangle$ between the linear and angular velocities of a diffusing chiral or achiral molecule. The new method of "spin chiral dichroism" is introduced as a practical way of promoting absolute asymmetric synthesis in prochiral reactions.

1. Introduction

Chirality has recently been defined by Barron [1] as being exhibited by systems that exist in two distinct enantiomeric states that are interconverted by space inversion but not by time reversal combined with any proper spatial rotation. This implies that the basic requirement for two collinear vectorial influences to generate true chirality is that one transform as a polar vector and the other as an axial vector and that both be time-even or both time-odd. Thus, in thermodynamic equilibrium [2] no combination of a static electric and static magnetic field can be effective in absolute asymmetric synthesis, i.e. in the use of an external chiral influence (in this context a combination of fields) to produce an enantiomeric excess in what would otherwise be the racemic product of a prochiral reaction mixture. (In a prochiral reaction mixture out of thermodynamic equilibrium, Barron has demonstrated [2] that in chiral media there is a breakdown of the principle of detailed balancing. In such "kinetically controlled" reactions, temporary absolute synthesis may be possible with false chiral influences, but only as long as the reaction remains out of thermodynamic equilibrium.)

Among true chiral influences are a combination of rotation and translation such as dissymmetric flow in a conical swirl, and the magneto chiral effect [3–5], a change in the value of the absorption coefficient of a chiral molecule due to a static magnetic field parallel or anti-parallel to the direction of propagation of electromagnetic radiation with wave vector $\boldsymbol{k}$. The magneto chiral effect is independent of the direction of polarisation of the electromagnetic field but changes sign on replacing the chiral molecule with its enantiomer, or on reversing the relative directions of the magnetic field $\boldsymbol{B}$ and propagation vector $\boldsymbol{k}$. Barron and Vrbancich [5] have suggested the name "magneto chiral dichroism" or "magneto chiral birefringence". According to Barron, a combination of $\boldsymbol{B}$ and $\boldsymbol{k}$ constitutes a true chiral influence by his definition of true chirality, mentioned above [5].

This Letter suggests a molecular dynamical mechanism that always accompanies the magneto chiral effect, which can be observed as a change in the power absorption coefficient or refractive index caused by the true chiral influence that is the result of symmetry breaking in the frame (X, Y, Z) by a combination of $\boldsymbol{B}$ and $\boldsymbol{k}$. Here (X, Y, Z) is the laboratory frame of reference. The methods used to arrive at this mechanism are applicable in ensembles of chiral molecules at equilibrium, either liquids or compressed gases, and are based on the recent axiom [6] that molecular dynamical ensembles can be treated with the rules of group theory.

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2. Symmetry considerations

In the frame (X, Y, Z), described by the rotation reflection group $R_h(3)$ with irreducible representations

$$D_g^{(0)}, ..., D_g^{(n)}, \quad D_u^{(0)}, ..., D_u^{(n)}$$

thermodynamic ensemble averages, $\langle A \rangle$, have the same symmetry as the quantity being averaged, A. This axiom, recently introduced by Whiffen [6], has led to the evolution of "group theoretical statistical mechanics" [7–11] and to the systematic evaluation of time correlation functions of different types. The methods of group-theoretical statistical mechanics and those of computer simulations have been found to be in detailed agreement. In terms of gerade (g) and ungerade (u) D representations a cross-correlation function (CCF) such as $\langle \boldsymbol{v}(t)\, \boldsymbol{\omega}^{\mathrm{T}}(0) \rangle$ has the symmetry of its product of representations $\Gamma(\boldsymbol{v})\,\Gamma(\boldsymbol{\omega})$. Here $\boldsymbol{v}$ is the molecular centre of mass velocity, and $\boldsymbol{\omega}$ the angular velocity of the same molecule, and the superscript T indicates the transpose. The Clebsch–Gordan theorem [12] reveals that the symmetry of the CCF $\langle \boldsymbol{v}(t)\, \boldsymbol{\omega}^{\mathrm{T}}(0) \rangle$ is therefore a sum of three ungerade D representations

$$\Gamma(\boldsymbol{v})\,\Gamma(\boldsymbol{\omega}) = D_u^{(1)} D_g^{(1)} = D_u^{(0)} + D_u^{(1)} + D_u^{(2)}, \qquad (1)$$

a sum that includes the symmetry representation of the pseudoscalar, $D_u^{(0)}$, defined as being invariant to proper rotation in space of the complete sample but with no directional properties. A pseudoscalar changes sign [1] under the parity operation $\hat{P}$ and is the scalar product of an axial vector and a polar vector. The natural optical rotation observable is a time-even pseudoscalar, $D_u^{(0)}$, i.e. is invariant under the time-reversal operator $\hat{T}$ [1]. The symmetry in frame (X, Y, Z) of the cross correlation function $\langle \boldsymbol{v}(t)\, \boldsymbol{\omega}^{\mathrm{T}}(0) \rangle$ is therefore the sum of a pseudoscalar $D_u^{(0)}$, a polar vector $D_u^{(1)}$, ungerade to parity, and an ungerade tensor representation $D_u^{(2)}$. These are, respectively, the scalar, vector and tensor products of the polar vector $\boldsymbol{v}$ and the axial vector $\boldsymbol{\omega}$.

These symmetry considerations also apply to the simultaneous influence of $\boldsymbol{B}$ and $\boldsymbol{k}$ in the frame (X, Y, Z) on a liquid composed of chiral molecules. The symmetry representation of these vectors is

$$\Gamma(\boldsymbol{B}) = D_g^{(1)}, \quad \Gamma(\boldsymbol{k}) = D_u^{(1)},$$

$$\Gamma(\boldsymbol{B})\,\Gamma(\boldsymbol{k}) = D_u^{(0)} + D_u^{(1)} + D_u^{(2)}, \qquad (2)$$

and they consequently allow thermodynamic averages of the same symmetry to exist in the frame (X, Y, Z) at thermodynamic equilibrium. From Barron's definition [1], a combination of these vectors applied simultaneously constitutes a true chiral influence, measurable through natural optical rotation with pseudoscalar symmetry $D_u^{(0)}$. If Barron's definition is correct, the product of representations of $\boldsymbol{B}$ and $\boldsymbol{k}$ must include $D_u^{(0)}$. This is indeed the case:

$$\Gamma(\boldsymbol{k})^{(+)}\,\Gamma(\boldsymbol{B})^{(+)} = \Gamma(\boldsymbol{k})^{(-)}\,\Gamma(\boldsymbol{B})^{(-)} = [D_u^{(0)} + D_u^{(1)} + D_u^{(2)}]^{(+)},$$

$$\Gamma(\boldsymbol{k})^{(+)}\,\Gamma(\boldsymbol{B})^{(-)} = \Gamma(\boldsymbol{k})^{(-)}\,\Gamma(\boldsymbol{B})^{(+)} = [D_u^{(0)} + D_u^{(1)} + D_u^{(2)}]^{(-)}. \qquad (3)$$

The above four choices arise from the fact that the field directions of both $\boldsymbol{B}$ and $\boldsymbol{k}$ may be $(+)$ or $(-)$. Thus $\boldsymbol{B}$ is parallel to $\boldsymbol{k}$ if both vectors are labelled $(+)$ or both are labelled $(-)$. Conversely $\boldsymbol{B}$ and $\boldsymbol{k}$ are antiparallel if the signs of $\boldsymbol{B}$ and $\boldsymbol{k}$ are different. (Note that a superscript $(+)$ in this context signifies the relative directions of $\boldsymbol{B}$ and $\boldsymbol{k}$, and should not be confused with the label usually assigned to enantiomers on the grounds of the optical rotation at a given wavenumber.) The complete symmetry description of the magneto chiral dichroic effect must therefore be

$$[D_u^{(0)} + D_u^{(1)} + D_u^{(2)}]^{(+)}$$

or

$$[D_u^{(0)} + D_u^{(1)} + D_u^{(2)}]^{(-)}.$$

Simultaneous application of $\boldsymbol{B}$ and $\boldsymbol{k}$ results in thermodynamic averages of these symmetries. The overall symmetry is also changed from $(+)$ to $(-)$ by replacing one enantiomer by another. It follows that a true chiral influence also has the symmetry

$$[D_u^{(0)} + D_u^{(1)} + D_u^{(2)}]^{(+)}$$

or

$$[D_u^{(0)} + D_u^{(1)} + D_u^{(2)}]^{(-)}$$

and that it makes possible the existence of thermodynamic averages of this symmetry. The magneto chiral effect is therefore accompanied by the appearance of $\langle \boldsymbol{v}(t)\, \boldsymbol{\omega}^{\mathrm{T}}(0) \rangle$ in the laboratory frame

(X, Y, Z), as well as natural optical rotation and a change in the power absorption coefficient [1,3–5]. All nine elements of the CCF are symmetry allowed in general, including the diagonal elements represented by $\langle \boldsymbol{v}(t)\cdot\boldsymbol{\omega}^{\mathrm{T}}(0)\rangle$. We are led directly to the useful conclusion that natural optical rotation and shift in the power absorption are both associated with the appearance in the laboratory frame of $\langle \boldsymbol{v}(t)\,\boldsymbol{\omega}^{\mathrm{T}}(0)\rangle$. (Note that the Faraday effect does not induce $\langle \boldsymbol{v}(t)\,\boldsymbol{\omega}^{\mathrm{T}}(0)\rangle$ because it uses a magnetic field of $D_g^{(1)}$ symmetry.)

3. Other true chiral influences in absolute asymmetric synthesis

A true chiral influence of the above symmetry will result in a surplus of enantiomers when applied to a prochiral reaction mixture at true thermodynamic equilibrium. The magneto chiral effect is therefore potentially useful in the synthesis of resolved enantiomers [1,4]. It would be useful to predict other practically applicable chiral influences by examining the D representations of applicable force fields in the frame (X, Y, Z). For example, if the liquid ensemble is subjected to an angular velocity $\boldsymbol{\Omega}$ and simultaneously to the propagation vector $\boldsymbol{k}$ we have the combined symmetry influence

$$\Gamma(\boldsymbol{\Omega})\,\Gamma(\boldsymbol{k}) = D_u^{(0)} + D_u^{(1)} + D_u^{(2)} . \tag{4}$$

Both vectors are odd under time reversal, so that a product of their time-reversal symmetries, denoted by

$$\hat{T}(\boldsymbol{k})\,\hat{T}(\boldsymbol{\Omega}) = (-)(-) = (+) \tag{5}$$

is even, as required by Barron's definition of chirality [1]. A true chiral influence is thus imparted to the prochiral reaction if the vessel containing the reaction mixture is spun about the axis containing $\boldsymbol{k}$. The latter takes effect usually at visible or ultraviolet frequencies, through photolysis, but other frequencies may also be used. Laser pulses would reduce heating or decomposition. An excess of enaniomers of one type is expected from the combined symmetry

$$\Gamma(\boldsymbol{\Omega})^{(+)}\,\Gamma(\boldsymbol{k})^{(+)} = [D_u^{(0)} + D_u^{(1)} + D_u^{(2)}]^{(+)} \tag{6}$$

and conversely for enantiomers of the mirror image type, produced by reversing $\boldsymbol{\Omega}$ relative to $\boldsymbol{k}$, i.e. by spinning the reaction vessel the other way or reversing the direction of the laser beam.

Alternatively, a true chiral influence may be generated by spinning an electric field around the sample and the laser beam, using an arrangement of electrodes. The spinning electric field has symmetry $D_g^{(1)}$ and angular velocity $\boldsymbol{\Omega}$. (Note that circularly polarised electromagnetic radiation is also a true chiral influence of this type, i.e. a combination of the wave vector $\boldsymbol{k}$ and a spinning electric field component of the electromagnetic field.)

4. Controversy concerning true chiral influence

In a recent review [1], Barron has discussed various claims [13–19] to effective absolute asymmetric synthesis. In D representations, the symmetry of any two-field chiral influence must be

$$[D_u^{(0)} + D_u^{(1)} + D_u^{(2)}]^{(+)}$$

or

$$[D_u^{(0)} + D_u^{(1)} + D_u^{(2)}]^{(-)} . \tag{7}$$

It must also be invariant to time reversal. The symmetry of a few commonly occurring vectors can be summarised as

$$\begin{aligned}
&\Gamma(\boldsymbol{B}) = D_g^{(1)}, \quad \hat{T}(\boldsymbol{B}) = \mathrm{u}\,;\\
&\Gamma(\boldsymbol{k}) = D_u^{(1)}, \quad \hat{T}(\boldsymbol{k}) = \mathrm{u}\,;\\
&\Gamma(\boldsymbol{E}) = D_u^{(1)}, \quad \hat{T}(\boldsymbol{E}) = \mathrm{g}\,;\\
&\Gamma(\boldsymbol{\omega}) = D_g^{(1)}, \quad \hat{T}(\boldsymbol{\omega}) = \mathrm{u}\,;\\
&\Gamma(\boldsymbol{v}) = D_u^{(1)}, \quad \hat{T}(\boldsymbol{v}) = \mathrm{u}\,;\\
&\Gamma(\boldsymbol{r}) = D_u^{(1)}, \quad \hat{T}(\boldsymbol{r}) = \mathrm{g}\,.
\end{aligned} \tag{8}$$

From this it follows that a true chiral influence is generated by products of representations such as the following

$$\begin{aligned}
&\Gamma(\boldsymbol{v})\,\Gamma(\boldsymbol{\omega}), \quad \Gamma(\boldsymbol{B})\,\Gamma(\boldsymbol{k}), \quad \Gamma(\boldsymbol{\Omega})\,\Gamma(\boldsymbol{k}),\\
&\Gamma(\boldsymbol{E})\,\Gamma(\dot{\boldsymbol{B}}), \quad \Gamma(\dot{\boldsymbol{E}})\,\Gamma(\boldsymbol{B}),\\
&\Gamma(\boldsymbol{\Omega})\,\Gamma(\boldsymbol{E})\,\Gamma(\boldsymbol{B}) .
\end{aligned} \tag{9}$$

Products such as $\Gamma(\boldsymbol{E})\,\Gamma(\boldsymbol{B})$ are not chiral. This affirms the view taken by Barron [1] that a combined use of a static electric field and a static magnetic field

at thermodynamic equilibrium [2] cannot constitute a true chiral influence, as asserted in the literature [13,14]. This confirms the criticisms [15–17] of these assertions at true thermodynamic equilibrium. Neither is the combination of the gravitational field and spin a true chiral influence, as asserted in the literature [18], because the symmetry of the gravitational field is even to $\hat{T}$.

To Barron's analysis of the literature we may now add the fact that a true chiral influence is accompanied in general by nine elements of the propeller function $\langle \boldsymbol{v}(t)\,\boldsymbol{\omega}^{\mathrm{T}}(0)\rangle$, which is even to $\hat{T}$ and odd to $\hat{P}$ [20–23]. The propeller function vanishes, however, at field-free quilibrium, or in the presence of a field or combination thereof which is even to $\hat{P}$, such as a static magnetic field. Some off-diagonal elements of the propeller function may exist in general in the presence of a static electric field of $D_u^{(1)}$ symmetry, in agreement with the computer simulations of the present author [24–26], using a Z axis electric field to generate

$$\langle v_X(t)\,\omega_Y(0)\rangle = -\langle v_Y(t)\,\omega_X(0)\rangle \qquad (10)$$

in the achiral dichloromethane liquid. In the more general case of an electric field with components in all three laboratory frame axes

$$\boldsymbol{E}=E_X\boldsymbol{i}+E_Y\boldsymbol{j}+E_Z\boldsymbol{k} \qquad (11)$$

the time dependence of the off-diagonal elements induced by the $D_u^{(1)}$ symmetry electric field will be

$$\begin{aligned}
&\langle v_X(t)\,\omega_Y(0)\rangle = -\langle v_Y(t)\,\omega_X(0)\rangle\,,\\
&\langle v_X(t)\,\omega_Z(0)\rangle = -\langle v_Z(t)\,\omega_X(0)\rangle\,,\\
&\langle v_Y(t)\,\omega_Z(0)\rangle = -\langle v_Z(t)\,\omega_Y(0)\rangle\,. \qquad (12)
\end{aligned}$$

A chiral influence of $D_u^{(0)}+D_u^{(1)}+D_u^{(2)}$ symmetry such as that generated by the magneto chiral effect always involves both a torque, generating $D_u^{(1)}$ symmetry in the cross correlation function, and a force, generating overall $D_u^{(0)}+D_u^{(2)}$ symmetry. This allows the diagonal elements of $\langle \boldsymbol{v}(t)\,\boldsymbol{\omega}^{\mathrm{T}}(0)\rangle$ to exist because the time CF $\langle \boldsymbol{v}(t)\,\boldsymbol{\omega}^{\mathrm{T}}(0)\rangle$ is finite. The combination of applied force and torque means that there is direct statistical correlation between the molecular $\boldsymbol{v}$ and $\boldsymbol{\omega}$ for $0<t<\infty$. (It is easy to see in a real propeller that $\langle \boldsymbol{v}(t)\cdot\boldsymbol{\omega}(0)\rangle$ exists in the laboratory frame because of the chiral (screw) symmetry of the propeller itself.) The existence of the nine elements can be checked straightforwardly with contemporary computer simulation, and this offers scope for detailed investigation.

In the experiment suggested by Baranova and Zel'dovich [19], the rotating electric field component of a low-frequency electromagnetic field is used to induce drift in opposite directions of the components of a racemic mixture. The symmetry of the rotating electric field component is $D_g^{(1)}$, and the low frequency means that $\boldsymbol{k}$ is not effective [27,28]. In this case, therefore, the radiofrequency electric field rotation does not constitute a chiral influence. This does not preclude non-equilibrium drift, where the sample is out of thermodynamic equilibrium and where the principle of detailed balancing no longer applies [2].

5. Estimate of magneto chiral birefringence and enantiomer advantage ratio

An estimate of the magnitude of magneto chiral birefringence has been given by Barron and Vrbancich [5], together with examples of material in which the effect is expected to be large. An experimental method was suggested based on the Rayleigh refractometer with magnetic fields applied in both arms. A conservative estimate gave a birefringence of $\approx 10^{-8}$, just within reach of the instrument. Using chiral samples with large rotational strengths, and intense magnetic fields, the theoretical birefringence can be increased, bringing it [5] within reach of the refractometer. Particularly favourable materials for observation include twisted dienes and helicenes, the tris(ethylene diamine)cobalt(III) ion, and the f–f absorption bands of chiral lanthanides and actinide complexes.

6. Estimate of the propeller effect due to spin chiral effects

It has been shown that a co-axial combination of propagation vector ($\boldsymbol{k}$) and spin ($\boldsymbol{\Omega}$) is a chiral influence. A practical implementation of this idea is to use a circularly polarised laser at infrared, microwave or radio frequencies to generate spin through the spinning electric field component of the electro-

magnetic field, as suggested by Baranova and Zel'dovich [19] and to implement $\boldsymbol{k}$ through a high-frequency unpolarised ultraviolet laser. This is likely to be far more efficient than actual physical spinning of the sample, or implementing a spinning electric field generated by electrode arrangements. In the available work of Baranova and Zel'dovich, an electric field strength $E=3\times10^5$ V m^{-1} at a frequency $\omega/2\pi=10^8$ Hz produced an estimate of local mean molecular velocity $\langle v\rangle=\pm0.7\times10^{-8}$ m s^{-1} generated by the propeller effect of a spinning electric field on a mixture of enantiomers. The field sent one enantiomer locally in one direction and the other locally in the opposite direction. The overall sample remains racemic, however, because the spinning electric field component of the circularly polarised radiofrequency electromagnetic field is not in itself a true chiral influence, as discussed by Barron [1]. In the present context, the effect of the co-axial ultraviolet laser with wave vector $\boldsymbol{k}$ would be to "lock in" the concentration excess $\Delta N/N$ of about 0.25% estimated by Baranova and Zel'dovich after an hour's application of a radiofrequency field. Excess concentrations of one type of enantiomer would be found in one end of the tube containing the liquid sample, concentrations which could be tapped off.

The role of the ultraviolet unpolarised laser would be to generate a true chiral influence, making possible the existence of $\langle v(t)\,\omega^{\mathrm{T}}(0)\rangle$ in the laboratory frame. In the experiment of Baranova and Zel'dovich this CCF must vanish overall, because the external influence considered by these authors (a spinning electric field) is not chiral [1] at true thermodynamic equilibrium [2].

These arguments are extendable to prochiral reaction mixtures, where the ultraviolet laser with wave vector $\boldsymbol{k}$ plays the extra, critically important, role of photolysis, i.e. breaking bonds and forming reaction products in a stereo-specific manner under the combined spin chiral influence of the two coaxial lasers. An excess of one type of enantiomer would be concentrated after sufficient treatment time in one end of the reaction tube. It is reasonable to assume a stationary mean gradient, defined by Baranova and Zel'dovich as the ratio of mean molecular drift velocity to diffusion coefficient of about 7% per cm. Computer simulations would improve on the diffusion model used by these authors.

7. Rayleigh refractometry

The methods and estimates provided by Barron and Vrbancich [5] for the magneto chiral effect can be used to measure, in principle, the spin chiral effect by replacing the magnetic fields in both arms of the Rayleigh refractometer by the spinning electric field component of a powerful circularly polarised electromagnetic field. The latter would be sent down the arms of the refractometer in opposite directions, in order to generate a birefringence. This can be done in principle by splitting the beam from the laser, and sending it down the arms of a Rayleigh refractometer using mirrors. The careful molecular property tensor analysis of Barron and Vrbancich, based on the concepts of Buckingham [29], would have to be repeated with a spinning electric field instead of the static magnetic field of the magneto chiral effect. It is possible, in principle, to use very intense laser pulses, generating spinning electric fields of magnitudes much greater than those considered by Baranova and Zel'dovich, for example, and in consequence, one can expect a measurable spin chiral birefringence in molecular liquids with large dipole moments, or in easily aligned material such as liquid crystals.

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References

[1] L.D. Barron, Chem. Soc. Rev. 15 (1986) 189.
[2] L.D. Barron, Chem. Phys. Letters 135 (1987) 1.
[3] G. Wagnière and A. Meier, Chem. Phys. Letters 93 (1982) 78.
[4] G. Wagnière, Z. Naturforsch. 39a (1984) 254;
G. Wagnière and A. Meier, Experientia 39 (1983) 1090.
[5] L.D. Barron and J. Vrbancich, Mol. Phys. 51 (1984) 715.
[6] D.H. Whiffen, Mol. Phys. 63 (1988) 1053.
[7] M.W. Evans, J. Mol. Liquids, to be published.

[8] M.W. Evans, J. Chem. Soc. Faraday Trans. II, submitted for publication
[9] M.W. Evans, Mol. Phys., submitted for publication.
[10] M.W. Evans, Chem. Phys., to be published.
[11] D.M. Heyes and M.W. Evans, in preparation.
[12] R.L. Flurry Jr., Symmetry groups, theory and applications (Prentice Hall, Englewood Cliffs, 1980).
[13] P. Curie, J. Phys. (Paris) 3 (1896) 393.
[14] P. Gerike, Naturwissenschaften 62 (1975) 38.
[15] H. Zocher and G. Török, Proc. Natl. Acad. Sci. US 39 (1953) 681.
[16] P.G. de Gennes, Compt. Rend. Hebd. Seances Acad. Sci. B 270 (1970) 891.
[17] C.A. Mead, A. Moscowitz, H. Weinberg and F. Meuwese, Tetrahedron Letters (1977) 1063.
[18] R.C. Dougherty, Origins Life 11 (1981) 71.
[19] N.B. Baranova and Yu. Zel'dovich, Chem. Phys. Letters 57 (1978) 435.
[20] M.W. Evans, Phys. Rev. Letters 50 (1983) 371.
[21] M.W. Evans, J. Chem. Soc. Chem. Commun. (1983) 139.
[22] M.W. Evans, J. Chem. Soc. Faraday Trans. II 79 (1983) 1811.
[23] M.W. Evans, Phys. Rev. A 30 (1984) 2062.
[24] M.W. Evans, Phys. Letters A 102 (1984) 248.
[25] M.W. Evans, Physica Scripta 31 (1985) 419.
[26] M.W. Evans, Physica B/C 131 (1985) 273.
[27] M.W. Evans, G.C. Lie and E. Clementi, Chem. Phys. Letters 138 (1987) 149.
[28] M.W. Evans, G.C. Lie and E. Clementi, Phys. Rev. A 36 (1987) 226.
[29] A.D. Buckingham, Advan. Chem. Phys. 12 (1967) 107.