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First-order quantum corrections to depolarized interaction-induced light-scattering spectral moments: Molecular-dynamics calculation

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A method for calculating the first quantum corrections to the moments of depolarized interaction-induced light-scattering spectra has been applied for a many-body system. Classical averages have been evaluated via the molecular-dynamics simulation technique. The numerical evaluation of the first quantum correction to a "static" and a "dynamical" property is given for simple fluids. We also find that systems which are usually considered classical from the point of view of static properties may exhibit a non-negligible quantum contribution to their "dynamical" behavior.

I. INTRODUCTION

In a recent paper,[1] hereafter referred to as I, we have derived, by means of the application of the Wigner method in quantum statistical mechanics,[2] expressions for the quantum correction up to $\hbar^4$ to the moments of a general spectrum. This theory, which has been developed for a many-body system of identical particles which obey Boltzmann statistics, is useful when exchange effects are negligible and the system is "almost classical" in the sense that the $\hbar$ series expansion of the property under consideration converges rapidly.

The main result of the theory developed in I is that the quantum corrections to the moments, for the case of a spectrum which is related to a correlation function of quantities which depend only either on the space coordinates $\{r\}$ or on the momentum coordinates $\{p\}$, can be written as classical averages and therefore calculated for a many-body system by means of a computer-simulation technique. Hansen and Weis[3] have applied the Monte Carlo method for the evaluation of the quantum corrections of a static property of a Lennard-Jones system, namely, the free energy, and then they have derived the behavior of the equation of state of neon near the triple point.

Here we will concentrate our attention on two properties of the depolarized interaction-induced light-scattering (DILS) spectrum, namely, the zeroth moment (integrated intensity) and the second moment. The first quantity, i.e., the integrated intensity, is of static nature and therefore the quantum behavior resembles what has been already found by Hansen and Weis. The other one, i.e., the second moment, reflects a dynamical aspect of the system; this is the first time that computer simulation of a classical system is applied to the determination of a property which is connected to the quantum-mechanical *dynamical* behavior of an N-body system. The calculation will show a great difference in the behavior of the first quantum correction to the "static" and "dynamical" quantities. We have here concentrated our attention only on the first quantum corrections to the DILS moments since our primary interest was (a) to verify, with the present computer facilities, the feasibility of the calculation of both the static and dynamical properties of an N-body system; and (b) to establish the order of magnitude of the quantum corrections. Moreover the long computational time which is required at present for that type of calculation prevented us, for the time being, to determine the next quantum correction of order $\hbar^4$. Since DILS experimental results are available,[4,5] and more work can be done further in systems where quantum corrections are non-negligible, it seems important to have the possibility of performing such a type of calculation. However, precise comparison with experimental results requires the determination of the convergence of the series expansion in $\hbar^2$ and therefore the calculation of at least the corrections up to $\hbar^4$.

Section II is devoted to the explicit derivation of the expressions of the first quantum corrections for the moments in terms of pair properties. In Sec. III we give the expressions of those quantum corrections for the DILS spectrum of a Lennard-Jones fluid in which only the lowest-order dipole-induced-dipole anisotropy of the interacting pairs is considered. Section IV deals with the description of the calculation of the previously mentioned quantities by means of the molecular-dynamics computer-simulation technique, while in Sec. V we discuss the result of the calculation when applied to the noble gases He, Ne, Ar, Kr, and Xe and to the molecular systems H_2 and CH_4.

II. THE FIRST QUANTUM CORRECTION TO THE MOMENTS

Let us consider a system of N identical particles in a volume V which obeys Boltzmann statistics. In this case the expressions for the zeroth and second moments M_0 and M_2 of a spectrum which is related to the self-correlation of a space variable $A(r)$ (r is the $3N$ dimensional space vector) have been derived in I and up to the first order in $\hbar^2$ can be written as

$$M_0 = M_0^{(0)} + \hbar^2 M_0^{(2)} , \tag{1}$$

$$M_2 = M_2^{(0)} + \hbar^2 M_2^{(2)} , \tag{2}$$

where

$$M_0^{(0)} = \langle A^2 \rangle , \tag{3}$$

$$M_0^{(2)} = \frac{1}{24m(kT)^2} \left[\frac{1}{(kT)} \langle A^2 (\nabla\Phi)^2 \rangle - 2\langle A^2 (\nabla\cdot\nabla\Phi) \rangle + M_0^{(0)} \langle (\nabla\cdot\nabla\Phi) \rangle \right] , \tag{4}$$

$$M_2^{(0)} = \frac{kT}{m} \langle (\nabla A)^2 \rangle , \tag{5}$$

$$\begin{aligned} M_2^{(2)} = {} & \frac{1}{24m^2(kT)^2} \langle (\nabla A)^2 (\nabla\Phi)^2 \rangle - \frac{1}{12m^2(kT)} [\langle (\nabla A)^2 (\nabla\cdot\nabla\Phi) \rangle - \langle (\nabla A \nabla A):(\nabla\nabla\Phi) \rangle] \\ & + \frac{1}{4m^2} \langle (\nabla\nabla A):(\nabla\nabla A) \rangle + \frac{1}{24m(kT)^2} M_2^{(0)} \langle \nabla\cdot\nabla\Phi \rangle , \end{aligned} \tag{6}$$

Φ is the total interaction potential, kT is the Boltzmann energy factor, m is the mass of one particle, ∇ and the dots mean vector gradient and scalar product, respectively, in the $3N$ dimensional space of the configurations of the N-particle system, and the averages are performed over the classical distribution function.

Let us assume now that both the interaction potential Φ and the DILS property A can be expressed in sums of pair contributions, namely,

$$A = \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j>i}}^{N} a(i,j) , \tag{7}$$

$$\Phi = \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j>i}}^{N} \phi(i,j) . \tag{8}$$

By defining

$$a(k,k) = \phi(k,k) = 0$$

the sum in (7) and (8) can be extended and made symmetric with respect to the indices. Thus we write

$$A = \tfrac{1}{2} \sum_{i,j=1}^{N} a(i,j) , \tag{7'}$$

$$\Phi = \tfrac{1}{2} \sum_{i,j=1}^{N} \phi(i,j) . \tag{8'}$$

With the pairwise additivity assumption the various expressions which appear in the $M_n^{(h)}$ can be written in terms of the properties $a(i,j)$ and $\phi(i,j)$ of the pair (i,j) and assume the form

$$(\nabla\cdot\nabla\Phi) = \sum_{i,j=1}^{N} \left[\phi''(i,j) + \frac{2\phi'(i,j)}{r(i,j)} \right] , \tag{9}$$

$$(\nabla A)^2 = \sum_{i=1}^{N} \vec{A}_1(i)\cdot\vec{A}_1(i) , \tag{10}$$

$$(\nabla\Phi)^2=\sum_{i=1}^{N}\vec{\Phi}_1(i)\cdot\vec{\Phi}_1(i)\;, \tag{11}$$

$$(\nabla A\nabla A):(\nabla\nabla\Phi)=\sum_{i=1}^{N}\vec{\mathrm{A}}_1(i)\cdot\overleftrightarrow{\Phi}_2(i)\cdot\vec{\mathrm{A}}_1(i)+\sum_{i,j=1}^{N}\vec{\mathrm{A}}_1(i)\cdot[\vec{\nabla}_i\vec{\nabla}_j\phi(i,j)]\cdot\vec{\mathrm{A}}_1(j)\;, \tag{12}$$

$$(\nabla\nabla A):(\nabla\nabla A)=\sum_{i=1}^{N}\overleftrightarrow{A}_2(i):\overleftrightarrow{A}_2(i)+\sum_{i,j=1}^{N}[\vec{\nabla}_i\vec{\nabla}_ja(i,j)]:[\vec{\nabla}_i\vec{\nabla}_ja(i,j)]\;, \tag{13}$$

where the prime and the double prime in Eq. (9) mean first and second derivative with respect to the argument, and $\vec{\nabla}_i$ is the three-dimensional gradient with respect to the ith particle. In Eqs. (10)–(13) the local tensorial functions $B(i)$, $\vec{\mathrm{B}}_1(i)$, and $\overleftrightarrow{B}_2(i)$, where B can be either A or Φ, are defined as

$$B(i)=\sum_{j=1}^{N}b(i,j)\;, \tag{14a}$$

$$\vec{\mathrm{B}}_1(i)=\vec{\nabla}_iB(i)\;, \tag{14b}$$

$$\overleftrightarrow{B}_2(i)=\vec{\nabla}_i\vec{\nabla}_iB(i)\;. \tag{14c}$$

It is worthwhile to notice that $\vec{\Phi}_1(i)$, as it has been defined, represents minus the force acting on the atom i due to the other $(N-1)$ atoms, so that Eq. (11) could also be written

$$(\nabla\Phi)^2=\sum_{i}\vec{\mathrm{F}}(i)\cdot\vec{\mathrm{F}}(i)\;. \tag{11'}$$

If a model form is given for the pair property $a(i,j)$ and the pair potential $\phi(i,j)$, the classical averages which appear in Eqs. (3)–(6) can be calculated via the molecular-dynamics (MD) computer-simulation technique and the first quantum corrections, for a many-body system, compared with the classical values of the moments.

III. MOMENTS OF THE DILS SPECTRUM IN A DID-LJ FLUID

From the general expressions we have given in the preceding section we can now evaluate the moments M_0 and M_2. For the potential we have chosen the familiar 6-12 Lennard-Jones (LJ) type, i.e.,

$$\phi(i,j)=4\epsilon\left[\left[\frac{\sigma}{r(i,j)}\right]^{12}-\left[\frac{\sigma}{r(i,j)}\right]^{6}\right]\;, \tag{15}$$

and for the property $a(i,j)$ we will assume a form which is proportional to the dipole-induced-dipole (DID) model of pair polarizability, namely,

$$a^{\alpha\beta}(i,j)=\left[\frac{\sigma}{r(i,j)}\right]^3\times\left[\delta_{\alpha\beta}-3\frac{r_\alpha(i,j)r_\beta(i,j)}{r^2(i,j)}\right]\;. \tag{16}$$

In the previous expressions $\vec{\mathrm{r}}(i,j)$ is the vector distance between the jth to the ith particle, $r(i,j)$ is its modulus, α and β label the Cartesian components x, y, z of the vectors, and $\delta_{\alpha\beta}$ is the Kronecker symbol. The expression for the pair property $a^{\alpha\beta}(i,j)$ has already been written in a reduced dimensionless form which is the most suitable for computer simulations. The parameters used for reduction are those of the Lennard-Jones potential, i.e., ϵ and σ. To be consistent we also define a reduced pair potential

$$\phi^*(i,j)=\frac{1}{\epsilon}\phi(r_{ij}/\sigma)\;,$$

temperature $T^*=kT/\epsilon$, density $\rho^*=\rho\sigma^3$, and gradient $\nabla^*=\sigma\nabla$. Moreover, if we define, following De Boer,[6] a reduced action Λ^* as

$$\Lambda^*=\frac{h}{\delta\sqrt{m\epsilon}}\;, \tag{17}$$

where m is the mass of a molecule, Eqs. (1) and (2) can be recast in reduced form as

$$M_0^*=M_0^{(0)*}+\left[\frac{\Lambda^*}{2\pi}\right]^2M_0^{(2)*}\;, \tag{18}$$

$$M_2=\left[\frac{\epsilon}{m\sigma^2}\right]M_2^*\;, \tag{19a}$$

$$M_2^*=M_2^{(0)*}+\left[\frac{\Lambda^*}{2\pi}\right]^2M_2^{(2)*}\;. \tag{19b}$$

Since we will be using only reduced units, the asterisks will be omitted in the following, and the expressions for the $M_n^{(h)}$ are given as

$$M_0^{(0)}=\langle(A^{\alpha\beta})^2\rangle\;, \tag{20}$$

$$M_0^{(2)}=\left\langle(A^{\alpha\beta})^2\left[\frac{1}{24T^3}(\nabla\Phi)^2-\frac{1}{12T^2}\nabla\cdot\nabla\Phi\right]\right\rangle+\frac{M_0^{(0)}}{24T^2}\langle\nabla\cdot\nabla\Phi\rangle\;, \tag{21}$$

$$M_2^{(0)} = T\langle(\nabla A^{\alpha\beta})^2\rangle \ , \tag{22}$$

$$M_2^{(2)} = \frac{1}{12T}\langle(\nabla A^{\alpha\beta}\nabla A^{\alpha\beta}):(\nabla\nabla\Phi)\rangle + \left\langle(\nabla A^{\alpha\beta})^2\left[\frac{1}{24T^3}(\nabla\Phi)^2 - \frac{1}{12T}(\nabla\cdot\nabla\Phi)\right]\right\rangle$$
$$+\tfrac{1}{4}\langle(\nabla\nabla A^{\alpha\beta}):(\nabla\nabla A^{\alpha\beta})\rangle + \frac{M_2^{(0)}}{24T^2}\langle\nabla\nabla\Phi\rangle \ , \tag{23}$$

and the quantities appearing in the above expressions take the reduced form which is reported in the Appendix. The above expressions (18)–(23) allow us to evaluate the first quantum corrections to the zeroth and second DILS moments for a Lennard-Jones fluid within the DID approximation and, most important, this calculation can be performed by means of classical MD.

Before discussing the details of the MD experiment it should be pointed out that even though we know that the LJ potential and the DID polarizability anisotropy are only rough approximations for describing the DILS spectrum of real fluids,[7,8] nevertheless, it is a necessary step to know the relative importance of the first quantum corrections to the spectral moments in order to discuss the problem of DILS in simple dense fluids. Moreover, the majority of the previous DILS MD calculations[9] of classical quantities have been performed with this model system, and therefore comparisons are better made within this approximation.

IV. THE MOLECULAR-DYNAMICS SIMULATION

Here in this section we will discuss the details of the MD computer simulation of the first quantum approximation to the first two even moments of the DILS spectrum in a fluid which interacts by means of a pairwise additive 6-12 Lennard-Jones potential [Eq. (15)] and whose total polarizability anisotropy is given by the sum of pair terms of DID type [Eq. (16)].

For the computer experiment we have chosen four different thermodynamic points, two in the liquid and two in the gas phase (see Table I), which should give a good overall picture of a Lennard-Jones fluid over the entire density range.

For the first point we set the reduced temperature and density to values which are close to the triple point. The second one was chosen in the liquid phase, on the liquid-vapor coexistence curve intermediate between the critical point and the triple point, and the third density was set equal to the critical density with a temperature slightly higher than T_c ($T_c = 1.35$, our T is 25% higher). With the potential parameters listed in Table II, the fourth point corresponds to He at room temperature and 366 amagat for which some experimental results exist.[4]

The computer experiment was performed with 108 atoms in a cubic box with periodic boundary conditions. The configurations were generated by using Verlet's algorithm with a reduced time step of 0.005 for states 1–3 and 0.002 for the high-temperature state. The cutoff used for the calculation of both forces and polarizabilities was always half the box length, i.e., 2.53, 2.81, 3.38, and 4.32, for states 1, 2, 3, and 4, respectively.

The experiments were done in part on a PDP 11/34 at the Prozeßrechenanlage Physik (zeroth moments) and in part on a CYBER 170-720 (second moments) of the Interuniversitäres EDV-Zentrum,

TABLE I. MD results in reduced units. The column of $\langle M_0^{(0)}\rangle_{\text{av}}$ is equivalent to $\frac{3}{4}S^{zz}$ as was defined by Alder *et al.*[9] The errors quoted are estimates based on the rate of convergence of $M_0^{(2)}$ and $M_2^{(2)}$.

ρ	T	$\langle M_0^{(0)}\rangle_{\text{av}}$	$\langle M_0^{(2)}\rangle_{\text{av}}$	Time steps	$\langle M_2^{(0)}\rangle_{\text{av}}$	$\langle M_2^{(2)}\rangle_{\text{av}}$ $\times 10^{-3}$	Time steps	$\dfrac{-M_0^{(2)}}{M_0^{(0)}}$	$\dfrac{M_2^{(2)}}{M_2^{(0)}}$	$\dfrac{M_2^{(2)}/M_2^{(0)}}{M_0^{(2)}/M_0^{(0)}}$
0.833	0.75	0.16	-1.5 ± 0.5	200 000	26	2.8 ± 0.1	10 000	9.69	107	11.0
0.61	1.15	0.40	-2.1 ± 0.7	100 000	49	2.0 ± 0.1	10 000	5.33	43.1	8.09
0.35	1.69	0.77	-3.4 ± 0.5	100 000	56	1.0 ± 0.1	10 000	4.35	18.07	4.15
0.167	27.6	1.01	-0.13 ± 0.03	60 000	947	0.9 ± 0.1	10 000	0.13	0.94	7.23

TABLE II. Reduction parameters and values of $(\Lambda/2\pi)$ for various simple systems. N_A is Avogadro's number. The values were taken from Hansen and McDonald (Ref. 10).

	He	Ne	Ar	Kr	Xe	H_2	CH_4
ϵ/K (K)	10.2	35.8	119.8	166.7	225.3	36.7	148.2
σ (Å)	2.556	2.75	3.405	3.68	4.07	2.959	3.817
$M=mN_A$ (g)	4.0	20.2	39.9	83.8	131.3	2.0	16.0
$(\Lambda/2\pi)^2$	0.182	0.008 87	0.000 875	0.000 256	0.000 099	0.0755	0.001 40

both at the University of Vienna.

The convergence of the second moment was satisfactory after 10 000 time steps in all four cases, while for the evaluation of the zeroth moment a much longer time had to be spent in order to obtain some degree of reliability. In fact, we had to run the experiment corresponding to the first thermodynamic state (triple point) for as long as 200 000 time steps while the second and third simulations were run for 100 000 time steps and the fourth for 60 000 time steps. Since a purely classical calculation of the zeroth and second moment requires a sample on the order of 10 000 and 1000 time steps, respectively, it is not surprising that the quantum corrections which essentially are fluctuations of these classical properties are more difficult to obtain. Table I shows the results which we obtained in units which are suitable for a comparison with other classical calculations. In fact, by multiplying both M_0 and M_2 by $(4/N)$, where N is the number of atoms used in the simulations, we find that $(4/N)M_0^{(0)}$ is identical to the quantity S^{xy} $(=\frac{3}{4}S^{zz})$ which was defined by Alder *et al.*[9] in DILS computer experiments. The quantities which are given in Table I are therefore defined as

$$\bar{M}_0=\frac{4}{N}M_0\ ,\quad \bar{M}_2=\frac{4}{N}M_2 \tag{24}$$

and are expressed in reduced units.

By comparing our triple-point value for $\langle M_0^{(0)}\rangle_{\text{av}}$ with the value of S^{zz} published by Alder *et al.*,[9] we find an excellent agreement in spite of the fact that we used only 108 atoms instead of 864. This is due to the fact that the cutoff on the local field was virtually the same in both calculations ($\sim 2.5\sigma$ at that density).

From Table I no immediate conclusion can be drawn since the value of the corrections depends upon Λ which in turn is a function of the molecular system under consideration. A thorough analysis of the results for a number of systems will be the subject of Sec. V.

V. RESULTS AND DISCUSSION

From the values reported in Table I and expressions (17)—(19) we can now evaluate the first quantum corrections of DILS moments for various systems at four thermodynamic states and therefore determine the importance of the quantum behavior with respect to the classical one for the properties we are concerned with. Table II gives the values of the parameters we have used to determine the value of Λ for the noble gases He, Ne, Ar, Kr, and Xe and the molecular systems H_2 and CH_4. We can then calculate, for the zeroth and second moments, the ratio between the values of the first quantum corrections and the classical parts. Table III gives the values of those ratios for the four thermodynamic states considered here. The first comment we can make on those results is that, since the ratio $M_2^{(2)}/M_2^{(0)}$ is between 4 and 11 times bigger than $M_0^{(2)}/M_0^{(0)}$ in all cases, the importance of the quantum-mechanical behavior on the dynamical properties is greatly magnified with respect to the static properties. This immediately leads to the fact that for systems like Ar and CH_4 which could be considered with very good approximation to be classical as far as static properties are concerned, there is a non-negligible quantum-mechanical contribution to the DILS second moment in the liquid phase since the first quantum correction here is between 4% and 15%, while even krypton and xenon near the triple point have corrections on the order of 3% and 1%. The same holds for He and H_2 at very high reduced temperature ($T=27.6$) where their second moment correction is 17% and 7%, respectively.

Low-temperature high-density He and H_2 show a completely quantum-mechanical behavior, as is well known; however, our results indicate that while for the static property a second-order calculation (up to the order $\hbar^4$) may give a satisfactory account of the quantum-mechanical behavior within Boltzmann statistics, for the second moment, quantum mechan-

TABLE III. Relative weight of the first quantum correction to the moments for various simple systems at four thermodynamic states.

	ρ	T	He	Ne	Ar	Kr	Xe	H_2	CH_4
$\frac{\hbar^2 M_0^{(2)}}{M_0^{(0)}}$	0.833	0.75	1.76	0.086	0.008	0.002	0.001	0.73	0.014
	0.61	1.15	0.97	0.047	0.005	0.001	0.001	0.40	0.007
	0.35	1.69	0.79	0.039	0.004	0.001	$<10^{-3}$	0.33	0.006
	0.167	27.6	0.024	0.001	$<10^{-3}$	$<10^{-3}$	$<10^{-3}$	0.010	$<10^{-3}$
$\frac{\hbar^2 M_2^{(2)}}{M_2^{(0)}}$	0.833	0.75	19.5	0.951	0.094	0.027	0.011	8.1	0.150
	0.61	1.15	7.8	0.382	0.038	0.011	0.004	3.3	0.060
	0.35	1.69	3.3	0.160	0.016	0.005	0.002	1.36	0.025
	0.167	27.6	0.17	0.008	0.001	$<10^{-3}$	$<10^{-3}$	0.071	0.001

ics is overwhelming. On the basis of what we have discussed here, we may say, as a final remark, that the present calculation demonstrates the importance of the quantum-mechanical behavior for the determination of DILS spectra in high-density low-temperature simple fluids, which will eventually show up for any type of system at sufficiently high frequency.

Moreover, it is also interesting to note that quantum corrections to the spectral moments appear to be, in principle, quite strongly dependent upon the form of the potential [Eqs. (4) and (6)]. This may show to be an important fact in comparison between theory and experiments where "real" potentials should be used.

APPENDIX

In this appendix we report the explicit expressions for the reduced quantities we need in order to calculate the quantum corrections to the zeroth and second spectral moments [Eqs. (20)–(23)].

We like to remember that α and β label the Cartesian components of the polarizability tensor, and the reduction parameters are those of the intermolecular potential. The parameter Z which has been introduced is defined as r/σ.

$$(A^{\alpha\beta})^2=\frac{1}{2}\sum_{i,j=1}^{N} a^{\alpha\beta}(i,j)\ , \tag{A1}$$

$$(\nabla\Phi)^2=\sum_{i=1}^{N}\vec{\Phi}_1(i)\cdot\vec{\Phi}_1(i)=\sum_{i=1}^{N}\vec{\mathrm{F}}(i)\cdot\vec{\mathrm{F}}(i)\ , \tag{A2}$$

$$[\vec{\mathrm{F}}(i)]_\alpha=\sum_{j=1}^{N}\left[\left(\frac{24}{Z^7}-\frac{48}{Z^{13}}\right)\frac{Z_\alpha}{Z}\right]_{Z=Z(i,j)}\ , \tag{A3}$$

$$(\nabla\cdot\nabla\Phi)=\sum_{i,j=1}^{N}\left(\frac{528}{Z^{14}}-\frac{120}{Z^8}\right)_{Z=Z(i,j)}\ , \tag{A4}$$

$$(\nabla A^{\alpha\beta})^2=\sum_{i=1}^{N}\vec{\mathrm{A}}_1^{\alpha\beta}(i)\cdot\vec{\mathrm{A}}_1^{\alpha\beta}(i)\ , \tag{A5}$$

$$[\vec{\mathrm{A}}_1^{\alpha\beta}(i)]_\gamma=-\sum_{j=1}^{N}\left[\frac{3}{Z^4}\left(\frac{Z_\alpha}{Z}\delta_{\beta\gamma}+\frac{Z_\beta}{Z}\delta_{\alpha\gamma}+\frac{Z_\gamma}{Z}\delta_{\alpha\beta}-5\frac{Z_\alpha Z_\beta Z_\gamma}{Z^3}\right)\right]_{Z=Z(i,j)}\ , \tag{A6}$$

$$\begin{aligned}(\nabla A^{\alpha\beta}\nabla A^{\alpha\beta}):(\nabla\nabla\Phi)={}&\sum_{i=1}^{N}[\vec{\mathrm{A}}_1^{\alpha\beta}(i)]\cdot[\overleftrightarrow{\Phi}_2(i)]\cdot[\vec{\mathrm{A}}_1^{\alpha\beta}(i)]\\&+\sum_{i,j=1}^{N}[\vec{\mathrm{A}}_1^{\alpha\beta}(i)]\cdot[\overleftrightarrow{\Phi}_{i,j}(i,j)]\cdot[\vec{\mathrm{A}}_1^{\alpha\beta}(j)]\ ,\end{aligned} \tag{A7}$$

$$[\overleftrightarrow{\Phi}_2(i)]_{\alpha\beta}=\sum_{j=1}^{N}[\overleftrightarrow{\Phi}_{i,i}(i,j)]_{\alpha,\beta}\ , \tag{A8}$$

$$[\overleftrightarrow{\phi}_{i,j}(i,j)]_{\alpha\beta}=-\left[\left(\frac{672}{Z^{14}}-\frac{192}{Z^{8}}\right)\frac{Z_\alpha Z_\beta}{Z^2}-\left(\frac{48}{Z^{14}}-\frac{24}{Z^{8}}\right)\delta_{\alpha\beta}\right]_{Z=Z(i,j)}, \tag{A9}$$

$$[\overleftrightarrow{\phi}_{i,i}(i,j)]_{\alpha\beta}=-[\overleftrightarrow{\phi}_{i,j}(i,j)]_{\alpha\beta}\ , \tag{A10}$$

$$(\nabla\nabla A^{\alpha\beta}):(\nabla\nabla A^{\alpha\beta})=\sum_{i=1}^{N}\overleftrightarrow{A}_2^{\alpha\beta}(i):\overleftrightarrow{A}_2^{\alpha\beta}(i)+\sum_{i,j=1}^{N}\overleftrightarrow{a}_{i,j}^{\alpha\beta}(i,j):\overleftrightarrow{a}_{i,j}^{\alpha\beta}(i,j)\ , \tag{A11}$$

$$[\overleftrightarrow{A}_2^{\alpha\beta}(i)]_{\gamma\delta}=\sum_{j=1}^{N}[\overleftrightarrow{a}_{i,i}^{\alpha\beta}(i,j)]_{\gamma\delta}\ , \tag{A12}$$

$$\begin{aligned}[\overleftrightarrow{a}_{i,j}^{\alpha\beta}(i,j)]_{\gamma\delta}=\Bigg[\frac{3}{Z^5}\Bigg\{&(\delta_{\alpha\beta}\delta_{\gamma\delta}+\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma})\\ &-\frac{5}{Z^2}(\delta_{\alpha\beta}Z_\gamma Z_\delta+\delta_{\alpha\gamma}Z_\beta Z_\delta+\delta_{\alpha\delta}Z_\beta Z_\gamma+\delta_{\beta\gamma}Z_\alpha Z_\delta+\delta_{\beta\delta}Z_\alpha Z_\gamma+\delta_{\gamma\delta}Z_\alpha Z_\beta)\\ &+\frac{35}{Z^4}Z_\alpha Z_\beta Z_\gamma Z_\delta\Bigg\}\Bigg]_{Z=Z(i,j)}\ ,\end{aligned} \tag{A13}$$

$$[\overleftrightarrow{a}_{i,i}^{\alpha\beta}(i,j)]_{\gamma,\delta}=-[\overleftrightarrow{a}_{i,j}^{\alpha\beta}(i,j)]_{\gamma,\delta}\ . \tag{A14}$$

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