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Citation for author's submitted version

Zhang, Yong-Hui, Tang, Li-Yan, Zhang, Xian-Zhou, Jiang, Jun and Mitroy, Jim (pre-print). Convergence of the multipole expansions of the polarization and dispersion interactions for atoms under confinement. Retrieved from <http://espace.cdu.edu.au/view/cdu:38226>

Citation for publisher's version

Zhang, Yong-Hui, Tang, Li-Yan, Zhang, Xian-Zhou, Jiang, Jun and Mitroy, Jim (2012). Convergence of the multipole expansions of the polarization and dispersion interactions for atoms under confinement. *Journal of Chemical Physics*, 136(17):174107-1-174107-6.

Notice: *The publisher's version of this work can be found at:*

<http://dx.doi.org/10.1063/1.4705279>

Convergence of the multipole expansion of the polarization interaction

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(Dated: August 2, 2011)

The multipole expansion of the polarization interaction between a charged particle and an electrically charged particle has long been known to be asymptotic in nature, i.e. the multiple expansion diverges at any finite distance from the atom. However, it is shown that the multipole expansion of the polarization potential of a confined hydrogen atom is absolutely convergent at a distance outside the atoms confinement radius. It is likely that the multipole expansion of the dispersion interaction of two confined atoms will also be absolutely convergent provided the internuclear separation of the two atoms is sufficiently large to exclude any overlap between the electron charge clouds of the two atoms.

PACS numbers: 34.20.Cf, 31.15.ap

I. NATURE OF THE POLARIZATION EXPANSION

The long-range interactions between a charged particle and an atom is usually described by a polarization potential. This interaction is constructed by making a multipole expansion of the two-particle coulomb interaction leading to the following long-range expression for the second-order adiabatic polarization potential,

$$V_{\text{pol}}(R) \sim - \sum_{\ell=1}^{\infty} V_{\text{pol}}^{(\ell)}(R) = - \sum_{\ell=1}^{\infty} \frac{\alpha_{\ell}}{2R^{2+2\ell}}. \quad (1)$$

In this expression, the α_{ℓ} are the static multipole polarizabilities. The most important term arising from $\ell = 1$, the static dipole polarizability is sometimes called the polarizability. Equation (1) has been long known to be an asymptotic expansion. The polarization potential given by Eq. (1) eventually diverges as ℓ increases at any finite value of R [1, 2].

Formal issues of a similar nature also lead to a problem in the multipole expansion of the atom-atom dispersion interaction. Dalgarno and Lewis [2] originally showed the multipole expansion of the H-H second-order dispersion interaction,

$$V_{\text{disp}}(R) \sim - \sum_{n=1}^{\infty} \frac{C_{4+2n}}{R^{4+2n}}, \quad (2)$$

also diverges in the Unsold mean energy approximation [3], as $n \rightarrow \infty$ at any finite R . Sometime later it was shown that the exact multipole series for the H-H interaction was also asymptotic [4, 5].

Recently, B-spline basis sets have become very popular for solving atomic structure and collisions problems [6–10]. Such methods often impose the boundary condition that the wave function is zero at some finite radial distance, i.e. effectively solving the Schrodinger equation in a sphere of finite volume. One aspect of bounding the

wave function is that the reaction of the wave function to an electric field also becomes bounded in space. This results in a multipole expansion of the polarization interaction that can be shown to be absolutely convergent provided that the distance from the atom is larger than the confining radius of the atom. The imposition of a $V = \infty$ boundary will result in a multipole expansion that is mathematically well behaved at the cost tolerating a small error in the size magnitude of the polarization potential.

In this manuscript the Unsold approximation is applied to estimate the multipole polarizabilities of a confined H atom. The resulting polarization expansion is then shown to be absolutely convergent when the radius is larger than the boundary of the confinement potential. This is supplemented by finite radius B-spline calculations of the hydrogen polarizabilities for a box size of $R_0 = 14 a_0$. The results of these explicit calculations confirm the Unsold analysis and it is shown that the error in the polarization potential arising from the use of finite radius polarizabilities does not exceed 3 part in 10^6 .

II. POLARIZATION INTERACTION FOR A CONFINED HYDROGEN ATOM

The static multipole polarizabilities of any spherically symmetric state are defined

$$\alpha_{\ell} = \sum_i \frac{f_{0i}^{(\ell)}}{(\Delta E_{0i})^2} \quad (3)$$

where ΔE_{0i} is the excitation energy from state 0 to state i , the sum implicitly includes the continuum, and $f_{0i}^{(\ell)}$ is the oscillator strength of multipole ℓ connecting the state 0 to the excited state i . The $f_{0i}^{(\ell)}$ are defined [11, 12]

$$f_{0i}^{(\ell)} = \frac{2|\langle \psi_0 \| r^{\ell} \mathbf{C}^{\ell}(\hat{\mathbf{r}}) \| \psi_i \rangle|^2 \Delta E_{0i}}{(2\ell + 1)}. \quad (4)$$

In this expression \mathbf{C}^ℓ is the spherical tensor of rank ℓ .

Consider the oscillator strength sum rule

$$S^{(\ell)}(0) = \sum_i f_{0i}^{(\ell)} \quad (5)$$

This satisfies the identity

$$S^{(\ell)}(0) = N \langle r^{2\ell-2} \rangle \quad (6)$$

[13] where N is the number of electrons and $\langle r^{2\ell-2} \rangle$ is a radial expectation value of the ground state wave function. This expression reduces to the well known Thomas-Reiche-Kuhn sum rule $S^{(1)}(0) = N$ for $\ell = 1$. For the hydrogen atom ground state, the sum rule is

$$S^{(\ell)}(0) = \frac{\ell(2\ell)!}{2^{2\ell-1}} \quad (7)$$

The exact value of the multipole polarizabilities for the hydrogen atom ground state can be written [14]

$$\alpha_\ell = \frac{(2\ell+2)!(\ell+2)}{\ell(\ell+1)2^{2\ell+1}} \quad (8)$$

For a confined atom, the radial expectation value in Eq. (6) will be bounded by the radius of the B -spline box, R_0 , i.e.

$$\langle r^{2\ell-2} \rangle \leq R_0^{2\ell-2}. \quad (9)$$

Note that the correctness of Eq. (6) for calculations in a finite box has been validated to 20 significant figures.

Eq. (9) shows the factorial growth in the sum-rule, Eq. (7) is eliminated once the wave function is confined. For the hydrogen atom ground state one has

$$S^{(\ell)}(0) \leq \ell R_0^{2\ell-2} \quad (10)$$

Confining a hydrogen atom also impacts the energies of the states. So the energies used to calculate the oscillator strengths and the energies used in the energy denominators of Eq. (3). As ℓ increases in size, the centrifugal potential will tend to dominate the coulomb potential for $r \leq R_0$. For $\ell > \sqrt{2Z}R_0$ the total potential is repulsive and increases monotonically for decreasing R . When this occurs, the minimum excitation energy will be larger than the potential at $R = R_0$, i.e. $\Delta E = \ell(\ell+1)/2R_0^2 - 1/R_0 + 0.5$. For sufficiently large ℓ one can write $\Delta E \approx \ell(\ell+1)/2R_0^2$.

Making the Unsold mean energy approximation [3], and setting the mean excitation energy to the minimum value, leads to the following large ℓ approximate expression for the hydrogen polarizabilities

$$\alpha_\ell \approx \frac{2R_0^{2\ell}}{(\ell+1)} \quad (11)$$

The ratio of two successive terms in Eq. (1),

$$T = \frac{V_{pol}^{(\ell+1)}(R)}{V_{pol}^{(\ell)}(R)} = \frac{(\ell+1)R_0^2}{(\ell+2)R^2} \quad (12)$$

This ratio is less than one for R_0/R less than 1. Therefore the polarization series is absolutely convergent as long as R is greater than R_0 .

This absolute convergence has been substantiated by calculations of the multipole polarizabilities of the hydrogen ground state. Calculations were performed using a B -spline basis with the outer boundary set to $R_0 = 14 a_0$ and results are reported in Table I. The static polarizabilities of hydrogen have been previously calculated using B -splines basis sets [15] but the intent of the present work is different from the earlier investigations.

The radial wave function is written as B -splines

$$\Psi(r) = \sum_i c_i B_i(r) \quad (13)$$

where $\Psi(r)$ is normalized such that

$$\int_0^\infty |\Psi(r)|^2 r^2 dr = 1. \quad (14)$$

The boundary conditions are such that the first B -spline is finite at the origin.

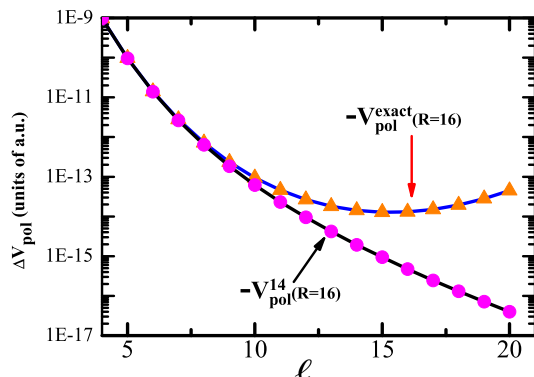


FIG. 1: The magnitude of the contribution to $V_{pol}(R = 16)$ from each successive multipole of Eq. (1). Results for $R_0 = 14 a_0$ and the unconfined atom are depicted.

The polarizabilities listed in Table I show the increasing difference between the the B -spline calculation of α_ℓ from the exact calculation at the higher values of ℓ . The polarizabilities are written as $\alpha_\ell^{R_0}$ where R_0 specifies the outer radius of the B -spline box. The B -spline $\alpha_\ell^{R_0}$ increases less rapidly than the exact value, α_ℓ^∞ , and at $\ell = 20$ is 1000 times smaller than the exact polarizability.

The convergence of the B -spline polarization potential at $R = 16 a_0$ is also shown in Figure 1. The contributions of each individual multipole in Eq. (1), i.e. $V_{pol}^{14}(R)$, are plotted as a function of ℓ . The divergence in the polarization series is apparent as the increments start to increase for $\ell \geq 15$. However, the increments steadily decrease as ℓ increases for the multipole expansion for the B -spline

TABLE I: The multipole polarizabilities (in a.u.) of the hydrogen atom ground state. Both exact and B-spline polarizabilities calculated in a sphere of radius $R_0 = 14 a_0$ are given. The polarization potential at $R = 16 a_0$ is computed with Eq. (1) including terms of successively larger ℓ for both sets of polarizabilities. The column E_{lowest} gives the lowest B-spline energies for each value of ℓ .

ℓ	E_{lowest}	α_ℓ^∞	α_ℓ^{14} : B-spline	$10^{-5} \times V_{\text{pol}}^\infty(R = 16)$	$10^{-5} \times V_{\text{pol}}^{14}(R = 16)$
1	-0.124540597990	4.500000000000000	4.499992173038246	-3.433227539062500	-3.433221567564579
2	-0.043113470410	15.000000000000000	14.99962361522554	-3.477931022644042	-3.477923929432083
3	0.011642665533	131.2500000000000	131.2214665586345	-3.479458973743021	-3.479451548358086
4	0.065428512840	$2.126250000000000 \times 10^3$	$2.123507410263223 \times 10^3$	-3.479555664398503	-3.479548114295026
5	0.122659506743	$5.457375000000000 \times 10^4$	$5.426703060742913 \times 10^4$	-3.479565358643910	-3.479557754056124
6	0.184625743002	$2.027025000000000 \times 10^6$	$1.988753009195520 \times 10^6$	-3.479566765175051	-3.479559134030737
7	0.251827759083	$1.026181406250000 \times 10^8$	$9.740932380195944 \times 10^7$	-3.479567043322079	-3.479559398059238
8	0.324490527950	$6.784199296875000 \times 10^9$	$6.020582918170891 \times 10^9$	-3.479567115152583	-3.479559461804639
9	0.402722627126	$5.671590612187500 \times 10^{11}$	$4.473394110827833 \times 10^{11}$	-3.479567138609732	-3.479559480306164
10	0.486577112031	$5.846894322018750 \times 10^{13}$	$3.838766302059065 \times 10^{13}$	-3.479567148055899	-3.479559486508025
11	0.576078316293	$7.284255842848359 \times 10^{15}$	$3.685245972773515 \times 10^{15}$	-3.479567152652911	-3.479559488833742
12	0.671234886264	$1.078630192114083 \times 10^{18}$	$3.862153915918611 \times 10^{17}$	-3.479567155311939	-3.479559489785837
13	0.772046602041	$1.872193833455160 \times 10^{20}$	$4.337864044592644 \times 10^{19}$	-3.479567157114797	-3.479559490203558
14	0.878508149199	$3.764357734467175 \times 10^{22}$	$5.150165059573718 \times 10^{21}$	-3.479567158530791	-3.479559490397286
15	0.990611293536	$8.679197301530880 \times 10^{24}$	$6.397025772360861 \times 10^{23}$	-3.479567159806084	-3.479559490491281
16	1.108346175117	$2.274460234018827 \times 10^{27}$	$8.248030398257013 \times 10^{25}$	-3.479567161111560	-3.479559490538623
17	1.231702096001	$6.722293580544535 \times 10^{29}$	$1.097317979742808 \times 10^{28}$	-3.479567162618750	-3.479559490563226
18	1.360668006907	$2.225432980085533 \times 10^{32}$	$1.499328767223332 \times 10^{30}$	-3.479567164567810	-3.479559490576357
19	1.495232809884	$8.201833248105232 \times 10^{34}$	$2.096237726358987 \times 10^{32}$	-3.479567167373771	-3.479559490583528
20	1.635385546034	$3.346738528714939 \times 10^{37}$	$2.990044876206528 \times 10^{34}$	-3.479567171846294	-3.479559490587524

$V_{\text{pol}}^{14}(R = 16)$ providing a computational demonstration of the absolute convergence of the B-spline expansion.

The imposition of the boundary at $R_0 = 14 a_0$ has resulted in a polarization potential that is 0.0003% smaller in magnitude at $R = 16 a_0$ than the expansion using the exact polarizabilities. Most of this difference arises from the dipole and quadrupole terms in the multipole expansion.

The demonstrated convergence of the B-spline expansion has some relevance to the earlier analysis by Brooks [16]. He stated that the origin of the multipole series divergence was the use of the expansion

$$V = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{k=0}^{\infty} \frac{r_{<}^k}{r_{>}^{k+1}} \mathbf{C}^k(\hat{\mathbf{r}}_1) \cdot \mathbf{C}^k(\hat{\mathbf{r}}_2) \quad (15)$$

beyond its region of validity. This analysis recommended that all radial matrix elements involved in the evaluation of the polarizability have their radial integrations limited to a finite value, e.g. X , which would be a lower bound on the region for which one writes the polarization potential using Eq. (1). The interaction, Eq. (15) is effectively reduced to

$$V = \sum_{k=0}^{\infty} \frac{r^k}{X^{k+1}} \mathbf{C}^k(\hat{\mathbf{r}}) \cdot \mathbf{C}^k(\hat{\mathbf{X}}) \quad (r \leq X) \quad (16)$$

where X is a lower bound to the radial coordinate used to evaluate V_{pol} . The resulting multipole expansion was then shown to be convergent. Brookes concluded that the divergence in the polarization expansion was caused by using Eq. (15) in regions of space where it is not correct.

This statement is correct, but cannot be used to imply that the evaluation of the second-order polarization interaction using $|\mathbf{r}_1 - \mathbf{r}_2|^{-1}$ without making the multipole expansion will lead to a convergent expansion in powers of R^{-1} . Indeed, it has been shown that by an exact analysis in the Unsold approximation that the power series expansion R^{-1} of the hydrogen atom polarization potential is asymptotic [1, 2]. However, using a wave function that is limited in radial extent, or using an interaction that is limited in radial extent [16] will lead to a convergent expansion of the polarization interaction.

III. CONCLUSION

It has been demonstrated that the multipole expansion of a confined hydrogen atom polarization potential leads to an inverse power series that is absolutely convergent provided the distance from the nucleus is larger than the box radius. While the result is rigorous for hydrogen, one can reasonably assert that the result can be applied to any atom. This result has implications that go beyond the second-order perturbation expansion of the polarization interaction. For example, the Stark effect is known to be divergent with respect to order of perturbation theory [17]. It is interesting to speculate whether bounding the wave function will also remove this divergence.

The multipole expansion of the atom-atom dispersion interaction is also known to be asymptotic in nature [2, 4, 5]. It is reasonable to speculate that this expansion would also be absolutely convergent for two confined

atoms provided the internuclear distance was larger than the sum of the two box sizes. It is interesting to note that Jansen [18] had suggested that the V_{disp} multipole expansion would converge provided the basis set used in the evaluation of the oscillator strength sum rule was restricted in dimension and range [18]. The numerical results associated with the work of Jansen were rather restricted in scope. Koide had devised a momentum space treatment that resulted in each dispersion parameter being multiplied by a radial cutoff of factor [19]. Although it could be shown that the resulting dispersion interaction was convergent at any finite R as $n \rightarrow \infty$ the method has only ever been applied to a few terms of the H-H dispersion interaction.

One aspect of the present analysis should be emphasised. Confining the atomic wave function to a finite region of space does constitute the imposition of an artificial constraint upon the wave function. However, such

constraints are routinely applied in calculations of atomic structure based on B-spline basis sets. These descriptions of atomic structure will automatically have no formal issues with respect to the convergence of the multipole expansion of the polarization interaction.

Acknowledgments

This work was supported by NNSF of China under Grant No. 10974224 and by the National Basic Research Program of China under Grant No. 2010CB832803. J.M. would like to thank the Wuhan Institute of Physics and Mathematics for its hospitality during his visits. The work of J.M was supported in part by the Australian Research Council Discovery Project DP-1092620.

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