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Effective Potential Energy Barriers and X-Ray Transitions of Sulphate Ion

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X-ray transition energies and intensities of sulphate ion are computed from limited CI wavefunctions including singly excited configurations. The results are interpreted in terms of one-electron promotions by using the improved virtual orbitals introduced first by Hunt and Goddard III [11]. The effective potential for virtual orbitals shows a barrier at large distance from sulphur nucleus.

Key words: X-ray transitions – Sulphur compounds

1. Introduction and Computational Procedure

It has been observed that the X-ray spectra of molecules of the type AX_n , where X are electronegative ligands surrounding a central atom A present often strong absorption bands both below and above the ionization limit (IP) of inner K or L electrons. These features have been interpreted as transitions from an inner, atomic like orbital to an excited molecular orbital [1, 2]. According to the picture proposed by Dehmer, the latter orbitals can essentially be of two types: diffuse orbitals which originate Rydberg type lines and compact orbitals concentrated within the molecular region, which are responsible for the strong lines. According to Nefedov [1] and Dehmer [2] the two kinds of orbitals are originated by an "effective potential barrier" due to the electronegative ligands X surrounding atom A. The effective potential should separate the excited orbitals in outer and inner well orbitals respectively, in close analogy with the situation occurring for *f* orbitals in rare earth ions [3].

Theoretical evidences for potential energy barriers in molecules were already found for BF_3 by Cadioli *et al.* [4] from *ab initio* SCF calculations. In this paper we have considered the sulphate ion whose X-ray spectrum, recorded by Nefedov and Fomichev [5], shows clearly the feature mentioned above. Since the experimental observations were made on the solid, a complete treatment taking proper account of the crystalline field, would involve quite laborious computations. As a preliminary step in this direction we carried out *ab initio* computations on the isolated ion SO_4^{2-} in order to obtain informations about its X transition energies

and intensities and to find evidences of the potential energy barriers assumed by Nefedov and Dehmer. The calculations were performed according to the following scheme. First of all a standard LCAO-SCF treatment has been performed, assuming a fixed tetrahedral geometry for SO_4^{2-} , with an S–O bond distance of 2.835 a. u. The basis consists of 36 contracted gaussians chosen to approximate a minimal basis of Slater type orbitals (STO) on each atom, implemented by 4s and 3d orbitals on sulphur. The orbital exponents ζ of STO's were given the values optimized by Clementi and Raimondi [6], except for 4s and 3d orbitals, where we have chosen $\zeta = 0.75$. In the case of 4s orbitals this value is very close to the free atom optimum value [7], and for 3d it is intermediate between the optimum values for atomic states arising from sp^3d^2 and s^2p^3d configurations [8]. Orbital exponents and contraction coefficients of gaussians were obtained by the method of McWeeny and Huzinaga [9]. All the oxygen STO's are expanded in three gaussians, while for sulphur the numbers of gaussians are: four for 1s, three for 2s, 2p, 3s, 3p, two for 4s and one for 3d orbitals respectively. The ground state configuration $1a_1^2 2a_1^2 1t_2^6 3a_1^2 2t_2^6 4a_1^2 3t_2^6 5a_1^2 4t_2^6 1e^4 5t_2^6 1t_1^6$ was found to have an energy of -691.767623 a. u. The calculation produced eleven virtual orbitals which were used to build the wavefunctions for excited states according to the following scheme. The inner atomic orbitals 1s, 2s, and 2p of sulphur were identified among the SCF MO's as $1a_1$, $3a_1$, and $2t_2$ respectively. The excited states are then divided in three groups, according to the vacancy in the inner shell, i.e. $1s^{-1}$, $2s^{-1}$, and $2p^{-1}$, corresponding to the spectroscopic designations K , L_I , and $L_{II,III}$ respectively. For each group all the singly excited singlet configurations where the proper inner orbital(s) is (are) replaced by each of the virtual canonical MO's are built. The linear mixing coefficients of configurations are obtained by solving the resulting secular equations, which also provide the values of excited states energies. Transition energies are obtained by difference with the SCF ground state energy, whose wavefunction, thanks to Brillouin's theorem [10], does not mix with excited states wavefunctions in this scheme. The procedure is therefore a limited CI, where all singly excited configurations, compatible with the orbital basis, with a fixed vacancy in an inner shell, are included. These wavefunctions could formally be described, in the language of group functions introduced by McWeeny [10], as a product of two groups. The first, representing a frozen core, collects all ground state orbitals except that, say ψ_i , bearing the vacancy, while the other group is built out of ψ_i and of all the SCF virtual orbitals. Thus orbital relaxation during the transition is accounted for only partially, i.e. only for virtual orbitals which are expected to be most sensitive to changes in the electron distribution.

The transition energies are listed in Table 1, together with ionization potentials of inner electrons of interest. For each transition is given the value of the oscillator strength f , computed according to the formula $f = (2/3) \Delta E \mu^2$, where ΔE and μ are the energy and electric dipole moment of the transition respectively, both expressed in a.u. A qualitative description of the transition in terms of orbital promotions is given in the last column. The CI wavefunctions of K and L_I states are linear combinations of singly excited configurations with a common vacancy in the non degenerate orbital $1a_1$ or $3a_1$. Therefore they can be rewritten as spin-projected single determinants involving one well defined excited orbital.

Table 1. Transition energies ΔE (eV) and oscillator strengths f for SO_4^{2-}

Inner shell vacancy	Excited state designation	ΔE	$f \cdot 10^3$	Qualitative description of the transition
$1s^{-1}$	1A_1	2503.8	0.0	
	1A_1	2509.3	0.0	
	1T_2	2510.8	1.3	$1s \rightarrow \text{antib. } S3p, O2s, O2p$
	1A_1	2512.9	0.0	
	1T_2	2514.6	0.1	$1s \rightarrow \text{antib. } S3p, O2s, O2p$
	1E	2515.0	0.0	
	2A_1	2500.3 (IP)	—	
$2s^{-1}$	1A_1	240.8	0.0	
	1A_1	246.6	0.0	
	1T_2	248.7	3.2	$2s \rightarrow \text{antib. } S3p, O2s, O2p$
	1A_1	250.9	0.0	
	1T_2	251.6	0.2	$2s \rightarrow \text{antib. } S3p, O2s, O2p$
	1E	252.0	0.0	
	2A_1	237.3 (IP)	—	
$2p^{-1}$	1T_2	178.5	0.004	
	1T_2	184.1	2.4	
	1T_2	186.1	0.4	
	1E	186.1	0.0	
	1T_1	186.2	0.0	
	1T_2	188.0	0.7	
	1A_1	188.4	0.0	
	1T_2	189.3	1.8	
	1T_1	189.3	0.0	
	1E	189.3	0.0	
	1T_2	189.6	1.0	
	1T_1	189.7	0.0	
	1A_1	189.9	0.0	
	2T_2	175.0 (IP)	—	

In this way the transition is described as a one electron promotion from the inner orbital $1a_1$ or $3a_1$ to a modified virtual orbital. The latter, because of the A_1 symmetry of the vacancy, is still a symmetry orbital.

In case of $L_{II,III}$ states, this reduction of the CI wavefunctions to a single configuration is no longer possible, since the vacancy is localized in the degenerate orbital $2t_2$. However, an approximate reduction is still feasible, according to the following considerations. The modified virtual orbitals used to describe the K and L_I states coincide with those defined by Hunt and Goddard III [11], Huzinaga and Arnau [12], and Davidson [13] who proposed to replace the Fock operator F by the following Eq. (1):

$$F' = F - (1 - \varrho) [J_i - 2K_i] (1 - \varrho) \quad (1)$$

where ϱ is the Fock-Dirac density operator of the SCF ground state and J_i , K_i are Coulomb and exchange operators associated with the MO φ_i bearing the vacancy. In the occupied subspace the eigenvectors of F' and F coincide, but they

do not in the virtual subspace. Equation (1) shows that the virtual eigenvectors of F' are subjected to a field of $N-1$ electrons distributed in all the occupied orbitals of the ground state but with a vacancy in ψ_i . Thus the substitution of F with F' corrects for a major shortcoming of the usual virtual orbitals, which feel a field of N electrons. However, if one uses directly Eq. (1) when the orbital ψ_i is degenerate, the operator F' is no longer totally symmetric and its eigenvectors are not symmetry adapted. For this reason we replaced formula (1) in case of $L_{II,III}$ states by:

$$F'' = F - 1/3 (1 - \rho) \left[\sum_{i=1}^3 (J_i - 2K_i) \right] (1 - \rho) \quad (2)$$

where i runs over three orthonormal components of the $2t_2$ manifold. The operator F'' is now totally symmetric, therefore its eigenvectors can be classified according to the symmetry group of the molecule. The promotion of one electron from a given component, e.g. ψ_1 of $2t_2$ to a ϕ involves the energy change given by Eq. (3):

$$E_1 = \varepsilon_\phi - \varepsilon_1 - 1/3 [2J_{1\phi} - J_{2\phi} - J_{3\phi} - 2K_{1\phi} + K_{2\phi} + K_{3\phi}] = \varepsilon_\phi - \varepsilon_1 + \delta_{1\phi} \quad (3)$$

where ε_ϕ and ε_1 are different eigenvalues of F'' . Equation (3) yields in general slightly different transition energies when a different member of the $2t_2$ manifold is used, the difference being given by $\delta_{1\phi}$. The latter quantities vanish when ϕ is of symmetry A_1 . The eleven transition energies were computed according to Eq. (3) and are collected in Table 2, together with the values of δ . In the same

Table 2. a) Symmetry designations, orbital energies (a. u.), transition energies and δ values from Eq. (3) (eV), mean radii (a. u.) of virtual orbitals from Eq. (2);
b) mean radii of basis functions referred to their centres (a. u.)

Symmetry	Orbital energy	Transition energy	δ	Mean radius
a)				
$6a_1$	0.127953	178.5	0.00	10.49
$7a_1$	0.335792	184.1	0.00	5.17
$6t_2$	0.421660	186.5	0.35	3.29
$8a_1$	0.481331	188.1	0.00	3.71
$7t_2$	0.526005	189.3	0.02	4.54
$2e$	0.538079	189.6	0.01	4.75
b)				
Orbital	Mean radius	Orbital	Mean radius	
$1s$ sulphur	0.11	$3p$ sulphur	2.04	
$2s$ sulphur	0.52	$3d$ sulphur	4.84	
$3s$ sulphur	1.75	$1s$ oxygen	0.22	
$4s$ sulphur	8.85	$2s$ oxygen	1.22	
$2p$ sulphur	0.45	$2p$ oxygen	1.22	

Table are also reported the mean orbital radii R_i for virtual orbitals and for basis functions, computed as $R_i^2 = \langle \psi_i | r^2 | \psi_i \rangle$. A comparison with the values reported in Table 1 for allowed transitions $L_{II,III}$ allows us to associate an excited orbital to each allowed transition, which will be now qualitatively described as a one electron promotion from $2t_2$ to one of the virtual orbitals. The latter can be divided into the symmetry species A_1 , T_2 , and E . The first A_1 orbital is essentially a very diffuse $4s$ sulphur orbital; its mean radius is larger than that of the parent atomic $4s$ function. This would correspond to an outer well state of Dehmer, and, accordingly, the f value of the associated CI transition is very small. The second A_1 orbital is associated with the most intense of the computed transitions, and it can be described as an antibonding MO built up mainly from sulphur $3s$ and oxygen $2s$ orbitals, with contributions from $4s$ and oxygen $2p$ orbitals. Its mean radius is considerably smaller than the previous one, but still larger than the S–O bond length (2.835). The last A_1 orbital is antibonding and involves $3s$ and oxygen $2p$ orbitals. Its low value of R shows that it is localized mainly within the molecular region and therefore it can be described as an inner well orbital. The orbitals of T_2 symmetry are built mainly out of $3p$, $3d$ and oxygen $2s$, $2p$ orbitals; $6t_2$ is a compact inner well orbital with dominant p character $7t_2$ is more diffuse with a large participation of sulphur $3d$ orbitals. $2e$ is a rather diffuse orbital built essentially out of sulphur $3d$ orbitals.

2. Comparison with Experiment

We like to stress that the present computations refer to an isolated sulphate ion and that the crystal field is likely to play a rather important role in transitions involving excited orbitals, especially those having high values of R . Therefore we expect to derive only qualitative indications concerning the experimental transitions.

We will be mainly concerned with $L_{II,III}$ transitions which have been more extensively treated in the literature [2, 5, 13]. According to the measurements by Nefedov and Fomichev [5], SO_4^{2-} shows three absorption maxima a , b , and c at 172.6, 181.6 and 191.5 eV in K_2SO_4 . The bands are rather broad and are likely to be a superposition of more transitions. The first band has been assigned by Dehmer [2] to a superposition of $2t_2 \rightarrow a_1^*$ (p -like) transitions, and the others to $2t_2 \rightarrow t_2^*$ (d -like) and $2t_2 \rightarrow e^*$ (d -like) transitions respectively. In Fig. 1 we have plotted a bar diagram of the computed f values versus transition energies. As a preliminary observation, there is a surprisingly good agreement between the computed and experimental value of sulphur $2p$ ionization potential. In Dehmer's paper this latter quantity seems to have been taken from a previous work by Vinogradov and Zimkina [14], who approximated it by averaging the values for SO_2 and SF_6 . If we take the ESCA values [15] for the binding energy of sulphur $2p$ electrons measured in gas phase, we obtain 178 eV, to be compared with a computed value of 175 eV. On the other hand, the binding energy of sulphur $2p$ electrons in solid Na_2SO_4 was found to be 168.9 eV by Lindberg *et al.* [16]. Since for a large number of sulphur compounds there is an approximately constant shift of ~ 6 eV between binding energies measured in gaseous and solid phase, we get ~ 175 eV for IP of sulphur $2p$ electrons referred to the "gaseous" phase.

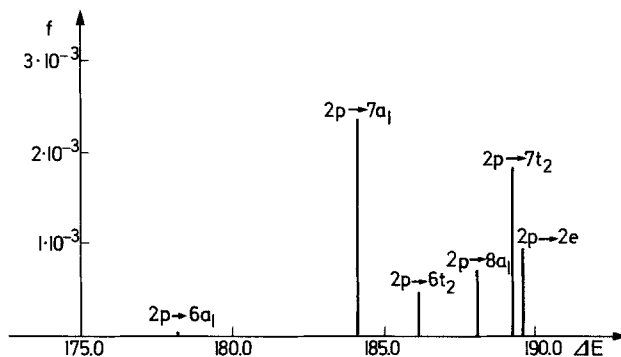


Fig. 1. Bar diagram of computed oscillator strengths versus transition energies (eV) for $L_{II,III}$ transitions

As far as transition energies are concerned, the comparison with experiment is far less favourable. If we discard our $2t_2 \rightarrow 6a_1$ transition in view of its low value of f , the sequence of computed transition energies roughly corresponds to that given by Dehmer, with the exception of $2t_2 \rightarrow 8a_1$ between $2t_2 \rightarrow 6t_2$ and $2t_2 \rightarrow 2e$. An assignment rigorously based on our computed energies would identify band c with the superposition $2t_2 \rightarrow 7t_2$ and $2t_2 \rightarrow 2e$ and band b with $2t_2 \rightarrow 7a_1$, in contrast with Dehmer's interpretation. However, it should be observed that the crystal field could modify considerably both transition energies and intensities, so that the present assignment can not be considered as definitive. To a first approximation, the nearest neighbours positive ions in the lattice are expected to provide an "outer well" in the potential which will especially perturb the orbitals of large size. Therefore a strong mixing among virtual orbitals of A_1 symmetry is likely to occur. Moreover this well could stabilize the "outer states" and eventually provide an interpretation for the band below the IP.

In the present computational scheme involving only singly excited configurations built up with virtual orbitals it is very unlikely that transition energies below the IP of the inner electrons are obtained. The energy of the highest occupied MO is already +2.95 eV, i.e. the SO_4^{2-} ion would gain energy by the removal of one electron from this orbital. This fact has been observed before in SCF computations of negative ions, and it should be kept in mind that unstable charged species are stabilized at least by the Madelung energy when placed in a crystal lattice.

It is important to point out that computed values of f are high enough to correspond to experimentally detectable lines. This is the only possible remark about K and L_T transitions, where the comparison with the scarce experimental data [5] is still more difficult.

3. Computation of the Effective Potential

The HF orbitals satisfy the one electron equation

$$-1/2 \nabla^2 \psi_i + U \psi_i = \varepsilon_i \psi_i, \quad (4)$$

where U includes nuclear attractions, Coulomb and exchange operators. Given an orbital ψ_i one can compute [17] from (4) a function $V(\mathbf{r})$ as in Eq. (5):

$$V(\mathbf{r}) = 1/2 \nabla^2 \psi_i / \psi_i + \varepsilon_i \quad (5)$$

and use it as a representation of the true non local potential U . This procedure has been applied before in similar problems [4, 17] and it has the advantage that it accounts for Coulomb and exchange effects as well. Equation (5) gives different functions $V(\mathbf{r})$ when applied to different orbitals ψ_i , while the idea of a potential barrier of Nefedov and Dehmer corresponds rather to a common potential for a set of excited molecular orbitals. Therefore we will look for a local approximation of U which holds for more than a single orbital ψ_i . Given a set of n equations of type (4), we impose to $V(\mathbf{r})$ the condition (6):

$$I = \iiint \sum_{i=1}^n [V(\mathbf{r}) \psi_i(\mathbf{r}) - U \psi_i(\mathbf{r})]^2 d\mathbf{r} = \text{minimum} . \quad (6)$$

If we regard U and the ψ_i 's as fixed, the condition $\delta I = 0$ gives:

$$V(\mathbf{r}) = \frac{\sum_{i=1}^n \psi_i(U \psi_i)}{\sum_{i=1}^n \psi_i^2} \quad (7)$$

which corresponds to a minimum, since $\delta^2 I = \iiint \sum \psi_i^2 d\mathbf{r} > 0$. The multiplicative components of U , i.e. nuclear attractions and Coulomb operators are left unchanged by Eq. (7), while the exchange operator is approximated by the function:

$$\sum_{i=1}^n \psi_i(\mathbf{r}_1) \sum_j \iiint \psi_j(\mathbf{r}_2) \psi_i(\mathbf{r}_2) r_{12}^{-1} d\mathbf{r}_1 \psi_j(\mathbf{r}_1) \left[\sum_{i=1}^n \psi_i^2(\mathbf{r}_1) \right]^{-1} \quad (8)$$

where index j runs over all the labels of occupied MO's. When also i runs over all the occupied MO's of a given system, Eq. (8) is nothing but the averaged exchange charge introduced by Slater [18] to simplify the HF equations.

In order to avoid cumbersome computations, one can replace U with the quantity $1/2 \nabla^2 \psi_i + \varepsilon_i \psi_i$ as in Eq. (7). This approximation amounts to consider Eq. (4) rigorously fulfilled, while in actual Roothaan-type SCF computations it holds only approximately. The same remark applies also to Eq. (5). The use of Eq. (7) has some advantages over Eq. (5). The latter defines a function which is singular near the nodes of ψ_i , and this can be rather disturbing for an highly excited ψ_i with many nodes. The function defined by Eq. (7) on the contrary will show a barrier only if there is a region of space where all the orbitals have low density and it will diverge to ∞ only in the very unlikely situation that all the orbitals considered have a common node. Function (7) will be in general smoother than (5), since the local deficiencies of ψ_i eventually overemphasized by (5) are averaged over a set of orbitals.

In Fig. 2 we show a plot of $V(\mathbf{r})$ averaged over all virtual eigenvectors of F'' (full line a). This curve is smooth and well behaved and shows something like a barrier on both sides of the C_3 axis, although at a very large distance (~ 7 a.u.) from sulphur nucleus. A similar barrier is also shown if we average over all eigenvectors of F''' ; the corresponding curve is not reported in the figure since it is very similar to this one. If one excludes from the average the very diffuse $6a_1$

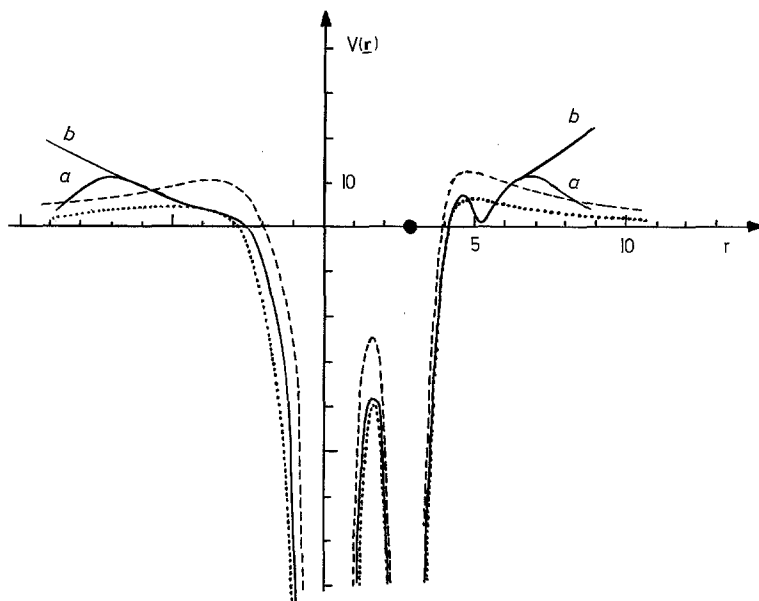


Fig. 2a and b. Plot of $V(r)$ (eV) versus distance r from sulphur nucleus along C_3 axis (a.u.). Full lines: (a) Eq. (7) averaged over all virtual orbitals; (b) $6a_1$ excluded from the average. Dashed line: Coulomb and nuclear contributions to the potential of the Fock operator F . Dotted line: Coulomb and nuclear contributions to the potential of modified Fock operator F'' in the virtual subspace. The position of oxygen nucleus is marked by a black circle

orbital, the plot of $V(r)$ matches curve a almost exactly in the region between the two main maxima, but continues to increase outside this region (full line b in Fig. 2). Thus, the appearance of a potential barrier is essentially dependent from the existence of the very diffuse $6a_1$ orbital which plays the role of outer well orbital, according to Dehmer's theory.

As far as the asymptotic behaviour of such curves for $r \rightarrow \infty$ it is concerned, it can be shown that $V(r) = O(r^{-2})$ when a gaussian basis is used to expand the MO's (see the Appendix). This feature can be of some relevance, in principle, in the regions of large r , although we think it does not matter very much here.

In the same Fig. 2 we have also plotted the sum of Coulomb and nuclear contributions to the effective potential U of Eq. (4). The dashed line is the representation of the multiplicative operator

$$C = 2 \sum_i J_i + \sum_A Z_A/r_A \quad (9)$$

where index i runs over all occupied orbitals and index A over all the nuclei in the molecule. In other words, the dashed line represents the electrostatic potential generated by all nuclei and electrons in the ground state of SO_4^{2-} . A maximum is evidenced at small distances from sulphur nucleus, as a result of the excess negative charge of the ion. Equation (9) does not represent satisfactorily the Coulomb potential for an occupied orbital ψ_k , since it contains also the self-repulsion

term J_k [11, 18]. For the modified virtual orbitals here used is more appropriate to consider, instead of Eq. (9), the operator:

$$C'' = C - 1/3 \sum_{j=1}^3 J_j \quad (10)$$

defined consistently with Eq. (2). The corresponding plot is given by the dotted line of Fig. 2. Therefore the barrier at large r shown by the full line a is not due to Coulomb effects, and, provided it is not a mathematical artifact due to the smallness of the basis set, it could support the concept of "effective potential barrier" proposed by Dehmer.

Appendix

Given a set of gaussian type functions $\{g_i(r)\}$ defined as in Eq. (A 1),

$$g_i(r) = (x - x_i)^l (y - y_i)^m (z - z_i)^n \exp(-\alpha_i r_i^2); \quad (A1)$$

$$r_i^2 = (x - x_i)^2 + (y - y_i)^2 + (z - z_i)^2$$

it is easy to show that the following equations hold:

$$\nabla^2 g_i = O(r^2) g_i, \quad r \rightarrow \infty, \quad (A2)$$

$$g_i = O(g_j) \quad \text{if } \alpha_i > \alpha_j, \quad r \rightarrow \infty. \quad (A3)$$

Suppose now that in the set $\{g_i\}$ there exists a single gaussian g_k having an exponential parameter α_k smaller than any other function in the set. This is actually true in our case, where g_k is one of the expansion functions of sulphur 4s orbital. Then, if ψ_m is a linear combination of the g_i 's, i.e. $\psi_m = \sum_{i=1}^N c_{mi} g_i$, one gets:

$$\nabla^2 \psi_m + \varepsilon_m \psi_m = O(r^2) g_k, \quad c_{mk} \neq 0, \quad (A4)$$

$$\psi_m = O(g_k), \quad c_{mk} \neq 0, \quad (A5)$$

$$\nabla^2 \psi_m + \varepsilon_m \psi_m = O(r^2) \circ (g_k), \quad c_{mk} = 0, \quad (A6)$$

$$\psi_m = O(g_k), \quad c_{mk} = 0. \quad (A7)$$

Equations (A4)–(A7) show that the averaged form of $V(r)$ derived from Eqs. (5) and (7) is a $O(r^2)$.

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