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Multipolar polarizabilities of the sodium atom by a variationally stable procedure

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We present a formalism that combines a semiempirical model potential with a second-order energy correction variationally stable method to evaluate the multipolar dynamic polarizabilities of the sodium atom. In this framework, the $\alpha_L(\omega)$ up to $L=4$ were calculated achieving good precision including the resonance domains of ω.

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I. INTRODUCTION

Multipolar polarizabilities are physical quantities of interest in the study of many physical and chemical phenomena.[1] An important example is the study of interactions among atoms, ions, and molecules with external radiation sources,[2] as in atomic beam experiments.[3–7] The multipolar polarizabilities at imaginary frequencies are used to determine dispersion coefficients of van der Waals interaction potentials,[8–12] which are related with the sign and magnitude of the scattering length associated with the stability and structure of Bose–Einstein condensates.[8,13] Recently the sodium atom multipolar polarizabilities have drawn interest due to a variety of theoretical and experimental investigations that rely on electronic and structure properties of its clusters,[14–18] and as a result of Bose–Einstein condensates for these atoms (Li, Na, Rb, and atomic hydrogen[8,13,19]). In this work we investigate the sodium structural properties by calculating the multipolar dynamic polarizabilities by a variationally stable procedure.

For atomic hydrogen and its isoelectronic sequence, analytical expressions have been established for the multipolar polarizabilities from second-order perturbation calculations.[20] The alkali metal atoms do behave, to some extent, as the hydrogen atom. The introduction of a model potential to describe the valence electron simplifies the atomic Hamiltonian, reducing the many-body problem to one optical active electron. The optical electron can fairly describe the atomic dynamics in radiative interaction processes,[21] assuming a Coulomb potential modified at short distances, with the inner electrons forming a polarizable closed-shell core. However, even with this simplifying representation, for precise calculations there is not a simple analytical expression for the multipolar polarizabilities, which requires a numerical approach. The standard procedure for the calculations involves matrix element diagonalization on the complete basis formed by the eigenfunctions of the atomic Hamiltonian. In order to obtain precise calculations it is necessary to account not only the bound states, but also the continuous configurations of the system.[1] As a result this method requires extensive calculations involving sums and integration over an infinite number of states, with the accurate representation of all states within the model potential approach.

In combining the model potential approach for the alkali metal atoms with a second-order energy correction variationally stable procedure,[22] the second-order perturbation is calculated in such a way that the convergence is obtained without the need of a complete basis expansion of the alkali atom eigenstates. Instead, Slater-type orbitals (STO) are used, where the unique configuration required for the calculation is the alkali atom ground-state wave function. The results are obtained from fast convergent algorithms and, consequently, with the reduction of the computational effort. The variationally stable procedure has been applied not only to the calculation of static and dynamic polarizabilities of atomic systems,[23,24] but also to the hydrogen molecule.[25]

The procedure described above is applied to the sodium atom with the ground-state wave function obtained solving the Schrödinger equation with the model potential from Ref. 26 (Sec. II A). The formalism of the procedure for the dynamic polarizability calculations is presented in Sec. II B. In Sec. III the results for the multipolar static and dynamical polarizabilities are presented, including the resonance region. Conclusions are presented in Sec. IV. Atomic units are used throughout the paper ($|e|=4\pi\varepsilon_0=m_e=\hbar=1$).

II. METHOD OF CALCULATION

In this section we introduce the model potential for the alkali metal atoms, which will be applied to the sodium atom, and the variationally stable procedure. The ground-

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TABLE I. Na$^+$ static multipolar polarizabilities.

$\alpha_L^c(0)$	α_1	α_2	α_3
Value (a.u.)	0.9457[a]	1.521[b]	7.5[c]

[a] Reference 60.
[b] Reference 61.
[c] Reference 9.

state wave function obtained will be used within the variationally stable procedure to evaluate the 2^L static and dynamic polarizabilities ($L=1,2,3,4$).

A. Model potential approach

To describe the motion of the valence electron for the alkali metal atoms a model potential based on the work of Liu and Starace[26] will be used. This model potential was originally developed for the photodetachment calculations of Na$^-$ and is explicitly given as

$$V(r) = -\frac{1}{r}[Z_c + (Z-Z_c)e^{-a_1 r} + a_2 r e^{-a_3 r}] - \frac{\alpha_1^c(0)}{2r^4}[f(r)]^2. \tag{1}$$

Besides the Coulomb potential, the short-range interactions are also included, being related to the partial nuclear shielding by the core electrons, and the spin-orbit coupling. The term, which contains the core (Na$^+$) static dipole polarizability $\alpha_1^c(0)$, is a long-range nonlocal contribution to the potential due to the core polarization effects. This potential considers the core symmetry perturbation under the influence of the valence electron. Higher-order polarization terms exist, but the major correction is due to the dipole term. The cutoff function is $f(r)=1-\exp[-(r/r_c)^3]$, which describes the decrease of the polarization interactions when the valence electrons penetrate into the core, being Z_c and r_c the core charge and radius, respectively. Many authors pointed out the importance of this polarization potential in corrections upon energies, oscillator strengths, and polarizabilities.[27–29] Furthermore, this correction was extended to all multipolar operators as

$$\tilde{d}_L = \sqrt{\frac{4\pi}{2L+1}}\left\{1 - \frac{\alpha_L^c(0)}{r^{2L+1}}[f_{2L+1}(r)]^2\right\}P_L(\cos\theta)r^L, \tag{2}$$

where $P_L(\cos\theta)$ is the Legendre polynomial of order L, and $\alpha_L^c(0)$ the static multipolar polarizability of the core, presented on Table I for the sodium atom and $f_{2L+1}(r)=1-\exp[-(r/r_c)^{2L+1}]$.

TABLE II. Sodium atom model potential parameters.

Parameter	Value (a.u.)[a]
a_1	3.324 424 528 010 140
a_2	0.713 727 982 135 612
a_3	1.832 818 151 516 440
r_c	0.524 506 379 602 377

[a] References 23, 31, and 32.

The set of semiempirical parameters $\{a_1, a_2, a_3\}$ and the core radius r_c are adjusted to reproduce the observable alkali spectra[30] for the Schrödinger equation $H\psi_{n\ell m}=E\psi_{n\ell m}$, where

$$H \equiv -\tfrac{1}{2}\nabla^2 + V(r), \tag{3}$$

$\psi_{n\ell m} \rightarrow y_{\ell m}(\theta,\phi)R_{n\ell}(r)$ and $V(r)$ is the model potential of Eq. (1). The set of coordinates $\{r,\theta,\phi\}$, and quantum numbers $\{n,\ell,m\}$ stands for the optical valence electron. In this way the ground state for the sodium atom is $3s$ ($\{n=3, \ell=0, m=0\}$). The semiempirical parameter values[23,31,32] of Na used in this work are shown on Table II.

The eigensolutions of the sodium atom were obtained using a variable-step numerical propagation of the wave functions.[33] To improve the precision and stability, the wave functions were propagated from small and asymptotic values of r using analytical solutions to a matching point where Cauchy conditions were imposed for the wave function and its first derivative. This model potential is simpler than other variations,[27,34–40] in which the semiempirical parameters are angular momentum dependent (ℓ of the valence electron). Although the potential has only a radial dependence, the semiempirical parameters were adjusted for all ℓ states.

B. Second-order perturbation variational approach

The effect on the sodium atom ground state caused by a multipolar electric field, as for the hydrogen atom, has no first-order perturbation energy corrections for the wave function $\psi_{n\ell m}$ using the model potential of Eq. (1). The multipolar polarizabilities, related to the second-order perturbation term, may be defined as $\alpha_L = 2\langle\psi_{n\ell m}^{(1)}|\tilde{d}_L|\psi_{n\ell m}^{(0)}\rangle$, where $\psi_{n\ell m}^{(0)}$ and $\psi_{n\ell m}^{(1)}$ are the first wave-function perturbation terms, respectively. Using the completeness of the wave-function basis and the corresponding initial-state energy E_i, the matrix elements become[2]

$$\alpha_L(\omega) = 2\sum_{n=0}^{\infty}\frac{|\langle\psi_{n\ell m}^{(0)}|\tilde{d}_L|\psi_i^{(0)}\rangle|^2}{E_{n,\ell}^{(0)}+\omega-E_i} + 2\int_0^{\infty}\frac{|\langle\psi_{k\ell m}^{(0)}|\tilde{d}_L|\psi_i^{(0)}\rangle|}{E_{k,\ell}^{(0)}+\omega-E_i}dk. \tag{4}$$

The integral is carried out on the continuum states of the sodium atom valence electron and the sum on the infinite bound states. On the other hand, the dynamical multipolar polarizabilities are also two-photon processes, which may

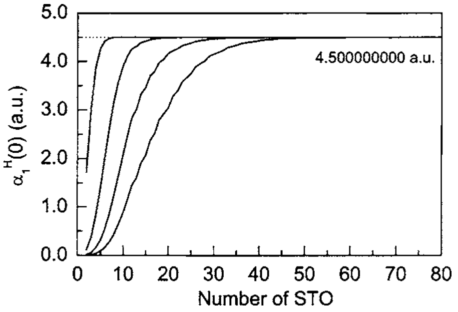

FIG. 1. Convergence of $\alpha_1^H(0)$ as a function of the number of Slater-type orbitals in the basis functions for selected values of the exponential parameter γ (0.2500, 2.250, 4.500, 7.750, and 9.000 a.u.).

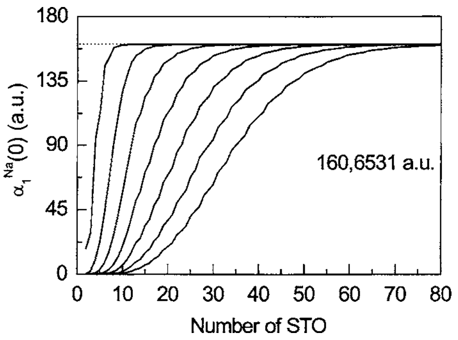

FIG. 2. $\alpha_1^{\mathrm{Na}}(0)$ convergence as a function of the number of STO basis elements M for selected values of the exponential parameter γ (1.500, 2.250, 3.500, 4.500, 6.000, 7.750, and 9.000 a.u.).

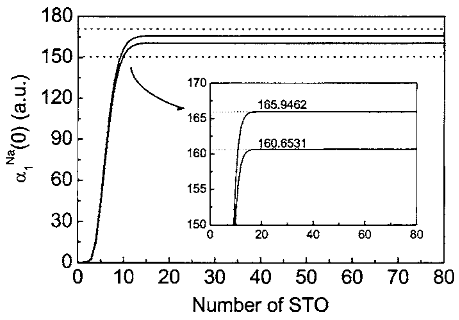

FIG. 3. Convergence of the static dipole polarizability of the sodium atom as a function of the number of STO basis elements M with exponential coefficient $\gamma=3.00$ a.u. The upper curve is obtained without core polarization corrections.

be defined as $\alpha_L(\omega)=-[T_{i\to i}^{(N=2)}(\omega)+T_{i\to i}^{(N=2)}(-\omega)]$ where the transition matrix is

$$T_{i\to i}^{(N=2)}(\omega)=\langle i|\tilde{d}_L\frac{1}{E_i+\omega-H}\tilde{d}_L|i\rangle. \tag{5}$$

Defining the ground state as initial wave function $|i\rangle \equiv|\psi_{n\ell m}^{(0)}\rangle$, the transition matrix can be represented within a variationally stable form in terms of an intermediate state $|\lambda\rangle$ as

$$T_{i\to i}^{(N=2)}(\omega)=2\langle i|\tilde{d}_L|\lambda\rangle-\langle\lambda|E_i+\omega-H|\lambda\rangle. \tag{6}$$

The intermediate state,

$$|\lambda\rangle\equiv\frac{1}{E_i+\omega-H}\tilde{d}_L|i\rangle, \tag{7}$$

can be represented as

$$|\lambda\rangle\equiv\frac{y_{\ell m}}{r}\sum_{\mu=1}^{M}a_\mu\phi_\mu(r), \tag{8}$$

where $\phi_\mu(r)=N_\mu r^{\ell+\mu}e^{-\gamma r}$ are Slater-type orbitals, and the normalization constant is

$$N_\mu=\sqrt{\frac{(2\gamma)^{2\ell+2\mu+3}}{\Gamma(2\ell+2\mu+3)}}. \tag{9}$$

The exponential coefficient γ is in principle an arbitrary positive parameter. In practice, γ is adjusted within a region for which the numerical calculation errors are reduced. The choice of Slater-type orbitals is based on the good convergence observed for the hydrogen atom (presented in Sec. III) and two-electron atom calculations.[23,24] However, unlike the analytical calculations of the matrix element angular part, the development of the radial integration proceeds by means of numerical calculations. For practical purposes, the precision achieved is very good with double precision variable-step integration processes.[33]

The matrix elements are obtained from the expressions

$$\langle i|\tilde{d}_L|\lambda\rangle=I(\ell m\ell' m' L0)\sum_{\mu=1}^{M}a_\mu N_\mu\int_0^\infty R_{n\ell}(r)d_L(r)r^{\ell+\mu}dr, \tag{10}$$

where $I(\ell m\ell' m' L0)$ is expressed in terms of $3j$ symbols as

$$I(\ell m\ell' m' L0)=(-1)^m\sqrt{(2\ell+1)(2\ell'+1)(2L+1)}\times\begin{pmatrix}\ell & L & \ell'\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\ell & L & \ell'\\ -m & 0 & m'\end{pmatrix}, \tag{11}$$

and $R_{n\ell}(r)$ is the radial part of the total wave function $\psi_{n\ell m}\to y_{\ell m}(\theta,\phi)R_{n\ell}(r)$ and $d_L(r)$ is the radial part of the multipolar operator defined in Eq. (2), and

$$\langle\lambda|E_i+\omega-H|\lambda\rangle=\sum_{\mu=1}^{M}\sum_{\mu'=1}^{M}a_\mu a_{\mu'}N_\mu N_{\mu'}\Bigg\{\left(E_i+\omega+\frac{\gamma^2}{2}\right)\frac{(2\ell+\mu+\mu')!}{(2\gamma)^{2\ell+\mu+\mu'+1}}+[Z_c-\gamma(\ell+\mu)]\frac{(2\ell+\mu+\mu'-1)!}{(2\gamma)^{2\ell+\mu+\mu'}}+(Z-Z_c)\times\frac{(2\ell+\mu+\mu'-1)!}{\left[\gamma\left(2+\frac{a_1}{\gamma}\right)\right]^{2\ell+\mu+\mu'}}+a_2\frac{(2\ell+\mu+\mu')!}{\left[\gamma\left(2+\frac{a_3}{\gamma}\right)\right]^{2\ell+\mu+\mu'+1}}+\frac{(\ell+\mu)(\ell+\mu-1)-\ell(\ell+1)(2\ell+\mu+\mu'-2)!}{(2\gamma)^{2\ell+\mu+\mu'-1}}+\int_0^\infty\frac{\alpha_L^c}{2r^4}[f(r)]^2r^{2L+\mu+\mu'}e^{-2\gamma r}dr\Bigg\}. \tag{12}$$

TABLE III. Comparison of the sodium atom static dipole polarizabilities with reported values from other authors.

Author(s)	$\alpha_1^{\mathrm{Na}}(0)$ (a.u.)	Author(s)	$\alpha_1^{\mathrm{Na}}(0)$ (a.u.)
This work	160.8522[a]	Marinescu *et al.* (Ref. 12)	152.9[a] (165.8[b])
This work	165.5873[b]	Spelsberg *et al.* (Ref. 63)	163.701
Mitroy and Bromley (Ref. 8)	161.8[c] (162.8[d])	Fuentealba and Reyes (Ref. 64)	162.0
Maroulis (Ref. 18)	166.02	Staton (Ref. 46)	167.5
Derivianko *et al.* (Ref. 11)	162.3[c] (163.0[d])	Sadlej and Urban (Ref. 47)	164.7
Lim *et al.* (Ref. 44)	166.12	Windholz and Musso (Ref. 65)	191.00
Patil and Tang (Ref. 62)	167.5	Molof *et al.* (Ref. 48)	159.3±4.3[e]
Patil and Tang (Ref. 2)	160.7	Hall and Zorn (Ref. 49)	164.7±11.5[e]
Mérawa and Rérat (Ref. 45)	166.002	Ekstrom *et al.* (Ref. 50)	162.7±0.8[e]

[a] Calculations with core polarization correction.
[b] Calculations without core polarization correction.
[c] Static dipole polarizability of the valence electron only.
[d] Static dipole polarizability of valence and core states.
[e] Experimental data.

III. RESULTS AND DISCUSSION

The matrix elements calculated from Eqs. (10) and (12) are used to evaluate the a_μ coefficients of an $M\times M$ linear system formed by the M component basis functions that represent $|\lambda\rangle$ [Eqs. (7) and (8)]. In this way it is possible to calculate the transition matrix elements $T_{i\to i}^{(N=2)}$, and finally obtain the frequency-dependent polarizabilities. The convergence of the polarizabilities is investigated with respect to M and the exponential parameter γ. In Fig. 1 the static dipole polarizability of atomic hydrogen is represented as a function of the number of Slater-type orbitals (M) in the basis functions for selected values of the exponential parameter γ (0.2500, 2.250, 4.500, 7.750, and 9.000 a.u.). The results confirm the choice of Slater-type orbitals for polarizability calculations, considering the fast convergence for a large range of γ. All calculations were carried out with a minimum of 2–80 Slater-type orbitals for the intermediate states $|\lambda\rangle$. The number of STO terms needed on the basis to obtain a predetermined precision is reduced as the value of γ becomes smaller. For the hydrogen atom, the static dipole polarizability converges to 4.5000 000 000 a.u., the expected result from analytical calculations.[20,41] The efficiency of the second-order variationally stable procedure may be compared to other methods. As an example, Yan *et al.*[42] have obtained $\alpha_1^H(0)=4.50$ a.u. using variational calculations with 70 terms, while the variationally stable procedure used in this work reproduces the same precision using 33 STO terms with $\gamma=3.00$ a.u.

The multipolar polarizabilities of the sodium atom (Fig. 2) have a similar convergence pattern as observed for the atomic hydrogen. Our result for the sodium dipole polarizability is $\alpha_1^{\mathrm{Na}}(0)=160.6531$ a.u. The effect of the core polarization correction on the dipole operator can be determined, as seen in Fig. 3, representing a 3% correction to $\alpha_1^{\mathrm{Na}}(0)$. This correction is important to the evaluation of multipolar polarizabilities as pointed out by many authors[27–29,34,43] and becomes more significant as the number of core electrons increases (increase of the core size). The values obtained for the sodium atom static polarizability are compared to results from other calculations and experimental measurements in Table III. These data are based on the work of Bonin and Kresin,[1] where the evolution on the calculations is presented.

To compare the results from theoretical calculations, it is practical to separate the dynamic multipolar polarizabilities as $\alpha_L(\omega)=\alpha_L^{\nu}(\omega)+\alpha_L^{c}(\omega)+\alpha_L^{c\nu}(\omega)$,[9] where the indices (ν,c) stand for valence and core electrons, while $c\nu$ accounts for the core-valence coupling contributions on the polarizabilities. As we treat only the valence electron explicitly, the results obtained are due to the valence electron and part of the core-valence coupling contributions. We have obtained

TABLE IV. Higher-order polarizabilities of the sodium atom ($L=2,3,4$).

Author(s)	$10^{-3}\times\alpha_2^{\mathrm{Na}}(0)$ (a.u.)	$10^{-4}\times\alpha_3^{\mathrm{Na}}(0)$ (a.u.)	$10^{-6}\times\alpha_4^{\mathrm{Na}}(0)$ (a.u.)
This work[a]	1.88247	5.58365	⋯
This work[b]	1.88487	5.58421	2.968 05
Mitroy and Bromley (Ref. 8)	1.880[c] (1.881[d])	5.7420[c] (5.7430[d])	
Safronova *et al.* (Ref. 51)	1.885(26)	5.54	
Patil and Tang (Ref. 2)	1807	5.430	2.965
Marinescu *et al.* (Ref. 12)	1878	5.5518	
Maeder and Kutzelnigg (Ref. 52)	1799	5.1167	

[a] Calculations with core polarization correction.
[b] Calculations without core polarization correction.
[c] Static dipole polarizability of the valence electron only.
[d] Static dipole polarizability of valence and core states.

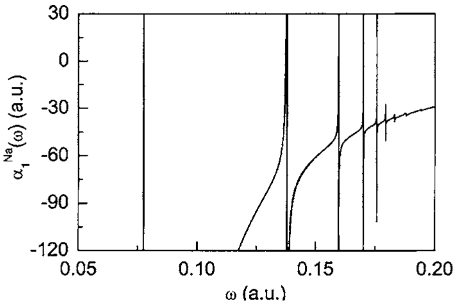

FIG. 4. Dipolar dynamic polarizability $\alpha_1^{\mathrm{Na}}(\omega)$ of Na.

160.6531 and 165.9462 a.u. for the sodium atom static dipole polarizability. In the former the core polarization correction is introduced on the multipolar operator. This result agrees with the recent work of Patil and Tang,[2] 160.7 a.u. They have used a model potential approach to determine asymptotic wave functions and have obtained analytical expressions for the transition multipolar matrix elements as well as to evaluate the multipolar polarizabilities. The results of Maroulis,[18] Lim *et al.*[44] Mérawa and Rérat,[45] Staton,[46] Sadlej and Urban,[47] and are in better agreement with our latter result (≈0.03%). These calculations evaluate the static dipole polarizability without core polarization correction. Mitroy and Bromley[8] have obtained 161.8 a.u. for the valence electron only, and 162.8 a.u. with *ab initio* many-body relativistic semiempirical calculations, which has been considered the most accurate one. With respect to this work, our result agrees within 0.59% (valence electron only) and 0.90% (total polarizability). Derivianko *et al.*[11] used a model potential approach and obtained 162.3 a.u., a value that predicts the whole dipole polarizability of the atom, even when treating explicitly only the valence electron. In order to obtain this result, Derivianko *et al.* adjusted the core polarizability in the core polarization correction of the multipolar operator to reproduce the experimental value of Molof *et al.*[48] There are other two experimental data for the static dipole polarizability. Hall and Zorn[49] measured $\alpha_1^{\mathrm{Na}}(0)$ with a deflection technique achieving 164.7±11.5 a.u. Ekstrom *et al.*[50] with an atom interferometry technique obtained the most accurate value of $\alpha_1^{\mathrm{Na}}(0)$. Accounting for statistical and systematic errors, their result is 162.7±0.8 a.u.

The higher-order static polarizabilities were obtained from the same variational processes. The fast convergence observed for the dipole calculations is maintained, as shown in Fig. 2. In Table IV the results are compared with values obtained by Patil and Tang[2] and others,[8,12,51,52] showing very good agreement.

With the inclusion of the photon frequency, the dynamic polarizabilities are also obtained using the variational approach, as shown in Fig. 4. The convergence with respect to the basis size is still rapidly achieved, allowing the determination of resonance positions. These energy positions coincide with the difference among the energy levels obtained from the direct solution of the atomic Hamiltonian. For each dynamic multipolar calculation the corresponding resonance is related to the allowed transition for the sodium atom as seen on Table V. For this reason, the 2^L dynamic polarizability calculation allows all $\Delta\ell = L$ transition resonance determination.

In general, after five resonances the inflection intensity, as shown in Figs. 4–6, decreases considerably, but the pre-

TABLE V. Comparison among resonance positions ($\omega_{i\to f}$ determined with the dynamic multipolar polarizabilities), experimental (Expt.), and several theoretical spectral lines of Rydberg states of the sodium atom.

Final state[a]	This work	MBPT[b]	SAC-CI[c]	TDCHF[d],[e]	Expt.[f]	Other values	$\|\Delta\|$ (%)[g]
$3p(^2P)$	0.077 495	0.077 312	0.0763	0.0714	0.077 298	0.0730,[h] 0.0774[i] 0.0772[j]	2.6(−1)
$4p(^2P)$	0.137 975	0.137 925	0.1368	0.1316	0.137 920	0.1320,[h] 1.387[i]	4.0(−2)
$5p(^2P)$	0.159 685	0.159 664	0.1581	0.1558	0.159 662	0.1606[i]	1.4(−2)
$6p(^2P)$	0.169 945	0.169 938		0.1641	0.169 941		2.4(−2)
$7p(^2P)$	0.175 615	0.175 607		0.1694	0.175 604		6.3(−3)
$8p(^2P)$	0.179 275	0.179 060			0.179 058		1.2(−1)
$3d(^2D)$	0.132 705	0.132 923	0.1317	0.1263	0.132 922	0.1340,[i] 0.1329[j]	1.6(−1)
$4d(^2D)$	0.157 305	0.157 600	0.1562	0.1574	0.157 416	0.1584[i]	7.1(−2)
$5d(^2D)$	0.168 715	0.168 734	0.1673	0.1619	0.168 753	0.1698[i]	2.3(−2)
$6d(^2D)$	0.174 865	0.174 905		0.1680	0.174 906		2.3(−2)
$7d(^2D)$	0.178 665	0.178 614		0.1717	0.178 613		2.9(−2)
$4f(^2F)$	0.157 465	0.157 600	0.1584		0.157 590	0.1586[i]	7.9(−2)
$5f(^2F)$	0.168 785	0.168 849	0.1681		0.168 847	0.1698[i]	3.7(−2)
$6f(^2F)$	0.174 915	0.174 964			0.174 963		2.7(−2)

[a] Transitions $3s(^2S) \to$ final state.

[b] Many-body perturbation theory from Ref. 53.

[c] Symmetry-adapted cluster—configuration interaction from Ref. 61.

[d] Time-dependent coupled Hartree-Fock from Refs. 62 and 63.

[e] Time-dependent coupled Hartree-Fock from Refs. 62 and 63.

[f] Experimental values from Ref. 30.

[g] $\Delta = 100\% (\omega_{i\to f} - \mathrm{Expt.})/\mathrm{Expt.}$. The number in parentheses corresponds to the power of ten.

[h] Modified relativistic Hartree-Fock from Ref. 58.

[i] Hartree-Fock with a polarized frozen core from Ref. 59.

[j] Third-order many-body perturbation theory with Dirac–Fock approach from Ref. 54.

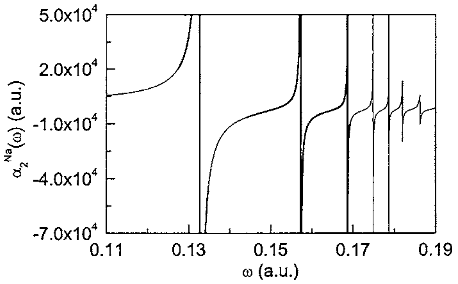

FIG. 5. Quadrupolar dynamic polarizability $\alpha_2^{\mathrm{Na}}(\omega)$ of the sodium atom.

cision aspect can be controlled by the inclusion of more STO in the basis functions or by the decrease of the frequency propagation step. All calculations were carried out with $\Delta\omega=0.0001$ a.u. and 80 STO in the basis functions. A smaller step would rise the computational time, an effort that does not worth the precision gained in resonance position considering the model potential approximations involved. The energy lines of the sodium atom Rydberg states obtained directly from the solution of the Schrödinger equation taking into account the model potential approach have a deviation of one part in 10^3 when compared with experimental results.[30] The resonance lines are less accurate than these energies ($\sim$1.0% difference), but still give rise to very accurate results (Table V). With respect to experimental energies, resonance lines have a mean precision of 6.2×10^{-2}%. Calculations using many-body perturbation theory (MBPT)[53,54] give more accurate results, with a mean precision value of a few ppm. In general, there is a gain in precision with respect to the principal quantum number. It should be noted that the MBPT calculations require large computational and time efforts, even for the sodium atom, a system of which relativistic and correlation corrections are not decisive contributions. The symmetry-adapted cluster configuration interaction[55] (SAC-CI) calculations are slightly less precise than the MBPT calculations and than the model potential approach itself. All these approaches give a significant accuracy increase in comparison with the Hartree–Fock[56–59] scheme. It should be noted that, regardless the calculations schemes considered, the model potential approach will lead to simplifying calculations due to its semiempirical character, but with reliable wave functions and devoid of considerable accuracy loss.

IV. CONCLUSION

The results presented in this work showed the efficiency of the model potential on the investigation of the sodium atom structural properties, along with the advantages of the second-order correction variational method. Although the determination of spectral lines is an important result for the atomic research, a complete approach demands precise wave functions as well. The strong correlation among the electrons within the core allows the study of the sodium atom as a one-electron system. Such characteristic is reflected by the accuracy of polarizability calculations performed with the model potential approximation. The application of the variationally stable method has shown to be numerically fast and reliable for all the dynamic multipolar calculations in this work. This procedure gives rise to a simple and fast approach for the calculation of polarizabilities since only the ground state was required on the calculations. It may be compared with the second-order perturbation approaches, which demand precise wave functions for a large number of bound and continuum states. The calculations were extended to the dynamic multipolar polarizabilities in order to proportionate results to the few found in literature, to which are shown to be in very good agreement.

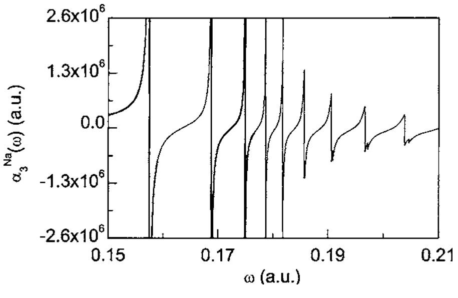

FIG. 6. Octupolar dynamic polarizability $\alpha_3^{\mathrm{Na}}(\omega)$ of the sodium atom.

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