PHYSICAL REVIEW A, VOLUME 63, 042511

# Quasirelativistic transition property calculations by the intermediate Hamiltonian method: Electronic transition dipole moments and radiative lifetimes in $Te_2$

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(Received 10 August 2000; published 20 March 2001)

We present a quasirelativistic method of *ab initio* calculations on molecular excited states and electronic transition moments within the relativistic effective potential approximation, based on the construction of intermediate Hamiltonians and spin-free one-particle transition density matrices by means of the many-body multipartitioning perturbation theory. The method is applied to describe the electronic transitions involved in the radiative decay of the $A0_u^+$, $B0_u^+$, and $B1_u$ states of $Te_2$. Good agreement of the computed transition dipole moment functions with their empirical counterparts is achieved. Theoretical radiative lifetime estimates for several low-lying rovibrational levels of the states under study are reported and compared with experimental collisionless lifetimes.

DOI: 10.1103/PhysRevA.63.042511 PACS number(s): 31.25.−v, 31.30.Jv, 33.70.Ca

## I. INTRODUCTION

The relativistic effective core potential approach [1,2] combined with the intermediate-coupling correlation treatment of the valence-electron subsystem provides a convenient framework for accurate *ab initio* studies on radiative electronic transitions in molecules containing heavy atoms. A straightforward way to solve the valence-electron problem through constructing configuration-interaction (CI) expansions of wave functions within the relativistic (double group) symmetry [3,4] leads to excellent results for small molecules but is not easily applicable to systems with a rather large number of electrons because of the rapidly increasing cost of calculations. Moreover, the double group CI generally suffers from a lack of size consistency. A promising alternative consists of developing and using quasirelativistic perturbative methods [2,5–7] that make use of the nonrelativistic ($\Lambda$-$S$) symmetry at the most time-consuming stages of calculations and reduce the size-inconsistency errors. A high reliability of electronic transition intensities obtained by one of the methods of this group has been demonstrated in recent papers [7,8]. In most cases, the exploitation of $\Lambda$-$S$ symmetries implies a partial contraction of the many-electron basis to a subset of low-lying eigenstates of the spin-averaged (scalar relativistic) Hamiltonian. This trick, which is also widely used in CI-like schemes [9–11], allows us to drastically reduce the computations in relativistic symmetries but gives rise to potentially dangerous convergency problems when large basis sets are employed [11].

The present paper formulates a quasirelativistic procedure of *ab initio* electronic structure and transition property calculations based on the construction of an intermediate (state-selective) effective Hamiltonian [12] and evaluation of spin-free transition density matrices by means of the many-body multipartitioning perturbation theory [13]. This procedure can be considered as a modification of the perturbative computational scheme proposed in Ref. [7]. It retains the numerical efficiency and approximate size consistency of the original version but avoids the partial contraction of wave functions after the scalar relativistic stage of calculations, thus ensuring a more adequate description of the interferences of correlations and spin-orbit interactions. Transition probabilities are estimated through the evaluation of transition electric dipole matrix elements. This approximation normally ensures an excellent accuracy of results concerning the spontaneous radiative decay of low-lying excited electronic states of molecules in the presence of $E1$-allowed channels, as well as field-induced $E1$-allowed light emission or absorption processes, provided that the intensity of the external electromagnetic field and transition energies are not too large. The use of direct transition density-matrix construction instead of the finite-field technique employed to evaluate transition dipole moments in Refs. [7,8] avoids cumbersome computations in symmetries lowered by the external field.

The method is applied to determine transition dipole moment functions and radiative lifetimes of excited electronic states of $Te_2$. This molecule provides an excellent test for relativistic theoretical approaches because of the complexity of its electronic structure, which is strongly affected by spin-orbit interactions [14], as well as the availability of detailed experimental information. $Te_2$ is a convenient object for molecular spectroscopy, serving as a wavelength standard, since tellurium vapor, being easily obtainable in quartz glass cells,

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1050-2947/2001/63(4)/042511(8)/$20.00

consists presumably of tellurium dimers exhibiting a dense pattern of intensive transitions in the visible and infrared spectral region. Energetic and radiative properties of $\mathrm{Te}_2$ have been studied intensively for a variety of low-lying molecular states correlating to ${}^3P_2+{}^3P_2$ and ${}^3P_2+{}^3P_{0,1}$ states of separated atoms (see, for example, [15–19] and references therein). The combination of existing experimental data on term values, lifetimes, fluorescence intensity distributions, and magnetic properties ($g$ factors [18,20] and Zeeman effect induced alignment-orientation conversion [19]) allowed to evaluate the intramolecular interaction parameters and to obtain deperturbed molecular constants and empirical Rydberg-Klein-Rees (RKR) $B0_u^+$, $B1_u$ potentials. As far as radiative properties are concerned, the carefully measured intensity distributions in high-resolution laser-induced fluorescence (LIF) spectra of $\mathrm{Te}_2$ have been used in Refs. [16,18,21] to deduce the dependences of transition strengths (transition moments) on the internuclear separation for eight-band systems. Lifetime measurements performed for several excited states [17,22–27] offered the possibility to estimate absolute transition moment values. At the same time, no reliable *ab initio* calculations of transition moment functions of $\mathrm{Te}_2$ can be found in the literature; moreover, the accuracy of *ab initio* potential-energy functions for the states above 10 000 $\mathrm{cm}^{-1}$ (i.e., those of particular importance for the LIF spectroscopy) obtained in Ref. [14] appears to be insufficient for most purposes because of severe limitations of the employed computational scheme. Reliable theoretical data concerning these states thus appear to be of interest.

In the present study, we restrict our attention to the transitions involved in the radiative decay of the $A0_u^+$, $B0_u^+$, and $B1_u$ (in earlier papers referred to as $A1_u$) states of $\mathrm{Te}_2$.

## II. METHOD

### A. Quasirelativistic intermediate Hamiltonians

We assume that the relativity is introduced through relativistic effective core potentials (REP's) and the total valence-shell Hamiltonian $H$ is split into the scalar part $h$ with spin-averaged REP's and the effective spin-orbit operator $w$ [1,28,29]. The latter operator is a sum of one-electron terms describing the spin-dependent deviation of the REP from the spin-averaged potential. Despite its one-body form, an effective spin-orbit operator extracted from all-electron full relativistic atomic reference calculations implicitly incorporates the atomic two-body spin-orbit contributions. Multicenter two-electron spin-orbit integrals are neglected, but this approximation is very reasonable because of the short-range nature of spin-orbit interactions [30]. The Hamiltonian is converted into a discretized form in a basis of Slater determinants built from the solutions of an appropriate scalar relativistic spin-restricted self-consistent-field–like problem.

Let us suppose that we are interested in $M$ lowest eigenstates $\{|\psi_\mu\rangle\}$, $\mu=1,\ldots,M$ (target $\Omega$ states) of the total relativistic Hamiltonian $H$ and proceed via the calculation of an intermediate (i.e., state-selective) quasirelativistic effective Hamiltonian $\tilde{H}$ in a model space $\mathcal{L}_P$ spanned by an appropriate subset of determinants $\{|J\rangle\}$. In contradiction with the commonly used state-universal (Bloch-Brandow) effective Hamiltonian approach [31], the model space dimension exceeds the number of target $\Omega$ states so that only a small number of $\tilde{H}$ eigenstates will be meaningful. To construct the model space, we first choose a reference set comprising the leading configurations of the target $\Omega$ states. The reference configurations should also dominate the expansions of $h$ eigenstates strongly overlapping with $\{|\psi_\mu\rangle\}$; these scalar eigenstates will be referred to as target $\Lambda$-$S$ states. Starting from the reference set, the model space is built by means of a conventional numerical perturbative selection procedure [32], which includes in $\mathcal{L}_P$ the configurations with potentially significant contributions to the target $\Lambda$-$S$ states.

In what follows, the spin-orbit interactions outside of the model space are neglected; in other words, we adopt the approximation

$$H\approx h+PwP, \tag{1}$$

where $P$ denotes the projector onto the model space. As has been pointed out in Refs. [29,33], the selection of $\Lambda$-$S$ configurations in the absence of the spin-orbit operator is obviously not the best way to ensure the validity of this approximation. However, the selection procedure [32] is known to favor the configurations with compact spatial electron distributions, which are of importance for a proper description of spin-orbit effects [11]. The reliability of the model (1) at least for compounds of rows $I$-$V$ of the main group elements has been demonstrated in numerous studies ([5,7] and references therein). Moreover, it can be adapted to studies of the sixth-row element compounds by means of an appropriate extension of the $\Lambda$-$S$ target manifold used in the selection [33].

The quasirelativistic intermediate Hamiltonian $\tilde{H}$ is approximated by the sum

$$\tilde{H}=\tilde{h}+PwP, \tag{2}$$

where $\tilde{h}$ is an intermediate Hamiltonian associated with the scalar Hamiltonian $h$ [12]. The lowest (''main'') eigenstates of $\tilde{h}$ should accurately reproduce the target $\Lambda$-$S$ energies and model-space parts of corresponding wave functions. At the scalar relativistic level of the treatment, a particular definition of the remaining (so-called intermediate) eigenstates of $\tilde{h}$ does not directly affect the results concerning the target $\Lambda$-$S$ states; only an indirect influence through convergency properties of computational schemes is possible [34]. In contrast, this definition becomes important for the related quasirelativistic problem (2) since the target eigensolutions can receive contributions from intermediate $\Lambda$-$S$ states because of the spin-orbit coupling. For instance, if the intermediate states incorporate no correlations associated with the coupling between the model space and its orthogonal complement (outer space), an energy gap between the main and intermediate $\tilde{h}$ eigenenergies will naturally cause an underestimation of the contributions from these states to the target $\Omega$ states. This problem is avoided in principle by introducing

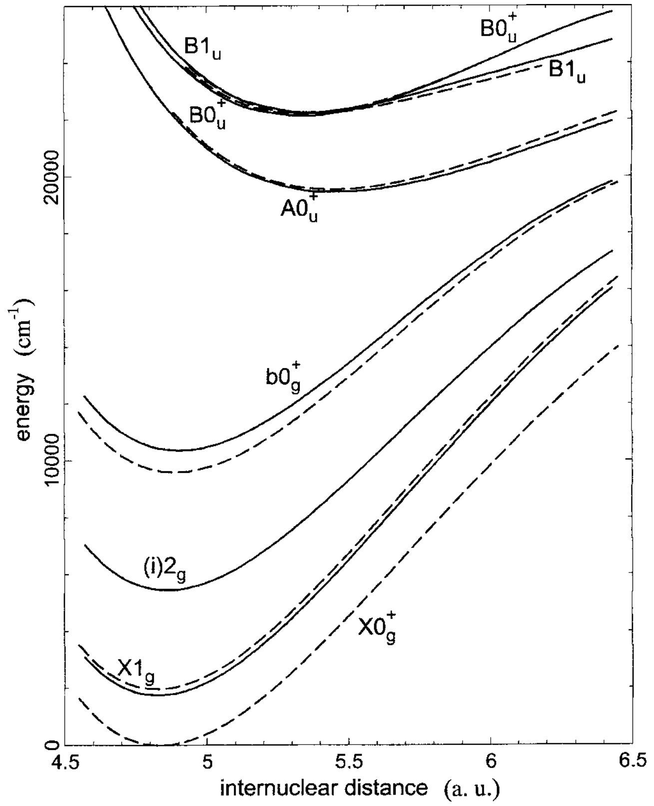

FIG. 1. Theoretical (solid lines) and empirical (dashed lines) potential energy functions of several electronic states of $Te_2$. Empirical data have been taken from Refs. [15] ($X0_g^+, X1_g, b0_g^+$), [45] ($A0_u^+$), and [18] ($B0_u^+, B1_u$).

fully correlated intermediate states, i.e., in passing to state-universal effective Hamiltonians [31]; one readily realizes that Eq. (2) holds automatically for a second-order state-universal effective Hamiltonian under the assumption (1). Unfortunately, the state-universal formulation of the theory is not compatible with the present choice of model spaces because of the famous intruder state problem [12]. A more reliable approach consists of using so-called dressed intermediate Hamiltonians, which provide a rather accurate correlated description of low-lying intermediate states and ensure a smooth decrease of accuracy when going up in energy [34,35].

In the present work, a dressed intermediate Hamiltonian is constructed by the spin-adapted many-body multipartitioning perturbation theory (MPPT), restricting the expansions after the second order. This approach is based on the simultaneous use of several quasi-one-electron zero-order Hamiltonians [13,36,37]. The Hermitian intermediate Hamiltonian matrix is defined by the formula

$$\langle J|\tilde{h}|J'\rangle = \langle J|h|J'\rangle + \frac{1}{2}\sum_{K:\ |K\rangle\notin\mathcal{L}_P}\langle J|h|K\rangle \times\left(\frac{1}{\Delta(J'\rightarrow K)}+\frac{1}{\Delta(J\rightarrow K)}\right)\langle K|h|J'\rangle, \quad (3)$$

where the energy denominators $\Delta(J\rightarrow K)$ are given by

TABLE I. Spectroscopic constants for several excited states of $Te_2$.

| | $T_e$ (cm$^{-1}$) | | $\omega_e(^{130}Te_2)$ (cm$^{-1}$) | | $r_e$ (Å) | |
|---|---|---|---|---|---|---|
| State | Theor. | Expt. | Theor. | Expt. | Theor. | Expt. |
| $X1_g$ | 1760[a]<br>2229[b] | 1975[c] | 248[a]<br>216[b] | 250[c] | 2.554[a]<br>2.66[b] | 2.552[c] |
| $(i)2_g$ | 5457[a]<br>6383[b] | | 235[a]<br>199[b] | | 2.573[a]<br>2.70[b] | |
| $b0_g^+$ | 10358[a]<br>10446[b] | 9600[c] | 227[a]<br>182[b] | 229[c] | 2.596[a]<br>2.73[b] | 2.587[c] |
| $A0_u^+$ | 19456[a]<br>17052[b] | 19451[d] | 138[a]<br>142[b] | 144[d] | 2.886[a]<br>3.25[b] | 2.882[d] |
| $B0_u^+$ | 22131[a]<br>21606[b] | 22203[e] | 165[a]<br>131[b] | 164[e] | 2.821[a]<br>3.03[b] | 2.824[e] |
| $B1_u$ | 22267[a]<br>22414[b] | 22217[e] | 155[a] | 152[e] | 2.837[a] | 2.840[e] |

[a] Present work.
[b] Reference [14].
[c] Reference [15].
[d] Reference [45].
[e] Reference [18].

$$\Delta(J\rightarrow K) = \sum_{r:\ N_r^K<N_r^J}(N_r^J-N_r^K)\epsilon_r^{\oplus} - \sum_{s:\ N_s^K>N_s^J}(N_s^K-N_s^J)\epsilon_s^{\ominus}. \quad (4)$$

Here $N_r^J$ and $N_r^K$ denote the occupancy of the $r$th spatial orbital in the model-space determinant $|J\rangle$ and the outer-space determinant $|K\rangle$, respectively. The entities $\epsilon_r^{\oplus}, \epsilon_s^{\ominus}$ are the nonrelaxed orbital ionization potentials and electron affinities with opposite signs, defined with respect to the model-space approximation for the target $\Lambda$-$S$ states and properly averaged [36] over all these states involved in the calculations.

The adopted ansatz (2) for the intermediate Hamiltonian enables us to take advantage of the nonrelativistic symmetry. The $\tilde{h}$ matrix has a simple block-diagonal structure with each nonzero block corresponding to a definite nonrelativistic spatial symmetry type and fixed total spin projection $S_z$. Only the blocks corresponding to the determinants with $S_z=0$ (or $S_z=\frac{1}{2}$ for a system with an odd number of electrons) are to be computed directly; the remaining nonzero $\tilde{h}$ matrix elements are then readily obtained by means of step-up and step-down spin operators $\hat{S}_+, \hat{S}_-$. At the same time, the present approach efficiently utilizes the information on the model-space spin-orbit interactions and properly describes their interplay with correlation effects due to an uncontracted nature of the computational scheme (the contributions of the model-space determinants to $\{|\psi_\mu\rangle\}$ are determined by the final diagonalization). It is worthwhile to compare it with the popular quasirelativistic method based on replacing the total spin-orbit (SO) operator by its projection onto the subspace

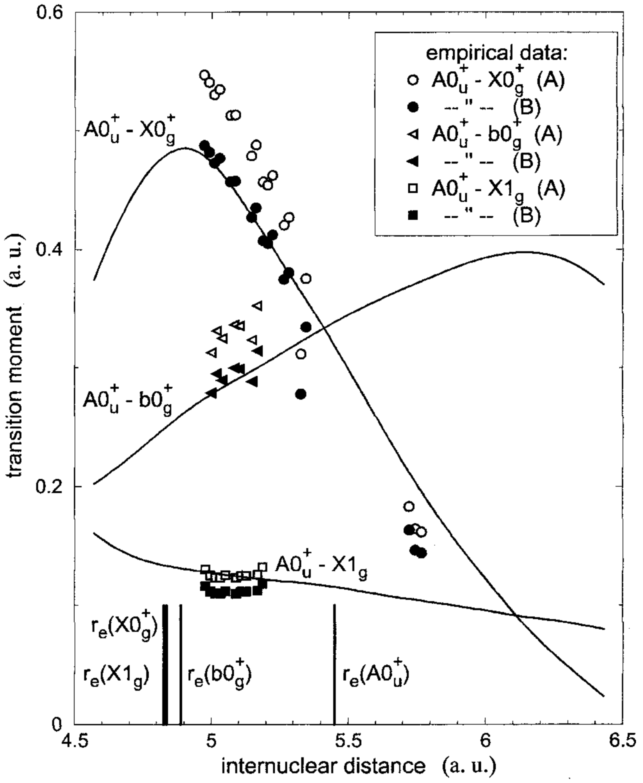

FIG. 2. *Ab initio* $A0_u^+ \rightarrow X0_g^+, X1_g, b0_g^+$ transition dipole moment functions (solid lines) and empirical transition moment estimates as functions of $r$ centroids [16] [$A$, empty symbols: original normalization corresponding to $\tau(A0_u^+, v'=11)=670$ ns; $B$, filled symbols: values renormalized to $\tau(A0_u^+, v'=11)=844$ ns [17]].

of low-lying eigenstates of $h$ [9]. The results of computations by the latter method with sufficiently small one-electron basis sets rapidly converge with the increase of the number of scalar eigenstates. However, one readily realizes that the representation of the SO operator in terms of bounded $h$ eigenstates is incomplete and one needs also to take into account the contributions from compact autoionizing states embedded into the continuum. Provided that the basis set is flexible enough to reproduce a large number of Rydberg-like states and finite-basis analogs of low-energy scattered states, which do not strongly interact with the low-lying states via $w$ but are located below the autoionizing states mentioned above, the convergence should become extremely slow. This problem does not arise in the present treatment since the contributions of all the model-space determinants to target $\Omega$ states are determined without any direct dependence on their weights in the expansions of target $\Lambda$-$S$ states. We should underline that the role of the latter states in our scheme is restricted to the spin-orbit-free configuration selection and evaluation of the MPPT ''orbital energies'' $\{\epsilon_r^{\oplus}\},\{\epsilon_s^{\ominus}\}$.

Let us finally notice that, by restricting the model-space spin-orbit interactions to the linear span of the main and low-lying intermediate eigenstates of $\tilde{h}$, one arrives at the quasirelativistic computational scheme employed in Refs. [7,8].

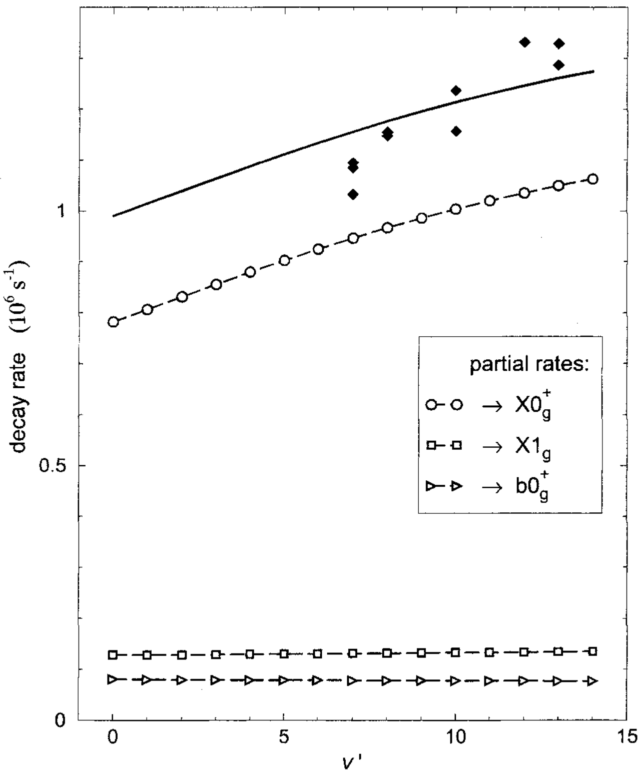

FIG. 3. Calculated partial (dashed lines) and total (solid line) radiative decay rates of $A0_u^+, v'$ states of $\mathrm{Te}_2$ ($J'=50$) as functions of the vibrational quantum number. Experimental collisionless lifetimes (Ref. [17]) for $J'=50\pm5$ are marked by filled diamonds.

### B. Transition dipole moment calculations

The diagonalization of $\tilde{H}$ yields the model-space parts $\{|\tilde{\psi}_\mu\rangle\}$ of the target relativistic wave functions $\{|\psi_\mu\rangle\}$. Provided that efficient ''diagrammatic'' algorithms are employed, no explicit approximation for the outer-space projections of $\{|\psi_\mu\rangle\}$ is obtained. A convenient way to incorporate the contributions from these projections to transition property values consists in a perturbative calculation of transition density matrices [38]. The first-order approximation for the spin-free $\mu \rightarrow \nu$ transition density matrix ${}^{\mu\nu}\rho$ compatible with the use of the intermediate Hamiltonian (2) and (3) is given by

$$
{}^{\mu\nu}\rho_{rs}=\langle\tilde{\psi}_\mu|\hat{E}_{sr}|\tilde{\psi}_\nu\rangle+\sum_{J,J':\ |J\rangle\in\mathcal{L}_P,|J'\rangle\in\mathcal{L}_P}\langle\tilde{\psi}_\mu|J\rangle\langle J'|\tilde{\psi}_\nu\rangle \times\sum_{K:\ |K\rangle\notin\mathcal{L}_P}\left(\frac{\langle J|\hat{E}_{sr}|K\rangle\langle K|H|J'\rangle}{\Delta(J'\rightarrow K)}+\frac{\langle J|H|K\rangle\langle K|\hat{E}_{sr}|J'\rangle}{\Delta(J\rightarrow K)}\right), \tag{5}
$$

cf. Ref. [39]. Here $\hat{E}_{sr}$ is the conventional spin-free one-electron excitation operator, which can be expressed in terms of the spin-orbital creation/annihilation operators as $\hat{E}_{sr}=a_{s\alpha}^{\dagger}a_{r\alpha}+a_{s\beta}^{\dagger}a_{r\beta}$. Since we neglect the spin-orbit coupling between the model space and the outer space, the matrix elements of the total Hamiltonian $H$ on the right-hand side of Eq. (5) are reduced to those of the scalar operator $h$, and we can still make use of the nonrelativistic symmetry during the calculation. The required dipole transition matrix elements $D_{\mu\nu}$ are immediately obtained as $\Sigma_{rs}{}^{\mu\nu}\rho_{rs}d_{sr}$, where $\|d_{sr}\|$ is the matrix of the one-electron electric dipole operator $d$ in the orbital basis. The direct construction of the $d$ operator compatible with the REP model for the quasirelativistic valence-shell Hamiltonian is not straightforward since the latter operator is not a large-component effective Hamiltonian of two-component all-electron theories. However, the problem is readily bypassed by defining the electric dipole as (minus) the first derivative of the Hamiltonian with respect to the intensity of the external uniform electric field. This definition is indirectly justified by highly accurate results of finite-field transition moment calculations in the framework of the REP approach [7,8]. In the present work, we restrict our attention to the field-independent (nonpolarizable) REP model and the differeniation of the Hamiltonian leads to the conventional (coordinate) form of $d$ (cf. Refs. [9,10]). Note that the incorporation of core polarization terms into REP would require us to employ more sophisticated electric-dipole operators.

### C. Details of computation

In the present study, we employed the *ab initio* shape-consistent REP of LaJohn *et al.* [28] for small (Kr-like) atomic cores of Te atoms, leaving 32-electron wave functions for explicit treatment. The valence Gaussian basis set $(6s6p7d2f)/[4s4p4d2f]$ was constructed from the outer part of the ''all-electron'' basis for electric property calculations [40] by reoptimizing a few larger exponential parameters for use with REP's and adding $f$ functions with exponential parameters 0.5602 and 0.2168. The molecular orbitals (MO) set was generated by concatenating the valencelike solutions of the Nesbet-Fock fractional-occupancy self-consistent-field problem $\cdots\sigma_g^{4/3}\pi_u^{8/3}\pi_g^{8/3}\sigma_g^{*4/3}$ for the neutral $Te_2$ molecule and higher-lying virtual orbitals of $Te_2^+$ with subsequent Gram-Schmidt orthogonalization; the procedure is similar to that used in Refs. [5], [7].

The scalar relativistic calculations were carried out in formal Abelian $D_{2h}$ symmetry, while only the inversion symmetry was taken into account during the spin-orbit treatment. All the $\Lambda$-$S$ states correlating with the two lowest nonrelativistic dissociation limits ($^3P+{}^3P$ and $^3P+{}^1D$) were considered as targets. At the selection step, the corelike $4d$ orbitals Te were kept doubly occupied. The model space comprised 1644–2249 Slater determinants with zero spin projection per $D_{2h}$ symmetry type; the corresponding total model-space dimension ($\dim\mathcal{L}_P$) was about $4.3\times10^4$. Additional single-point calculations demonstrated that the dipole moment estimates for intensive transitions are stable within 1–2% with respect to further extension of the model space (up to $\dim\mathcal{L}_P\approx7.6\times10^4$). The integral evaluation and transformation, as well as the spin-orbit-free configuration selection, were performed by the Toulouse program package PSHF-CIPSI. The $\tilde{H}$ eigenstates were determined by the modified Davidson method for complex matrices implemented in Ref. [29].

TABLE II. Calculated radiative lifetimes $\tau_{\mathrm{rad}}$ and measured total lifetimes $\tau$ (ns) for several $(v',J')$ levels of the $A0_u^+$, $B0_u^+$, and $B1_u$ states of $^{130}Te_2$.

| State | $v'$ | $J'$ | $\tau_{\mathrm{rad}}$ (Calc.) | $\tau$ (Expt.) | |
|---|---|---|---|---|---|
| $A0_u^+$ | 6 | 87 | 898 | 800±100 | [46] |
| | 7 | 41 | 863 | 920±18 | [17] |
| | 7 | 77 | 876 | 1047±26 | [17] |
| | 7 | 109 | 895 | 951±16 | [17] |
| | 8 | 41 | 848 | 939±26 | [17] |
| | 8 | 87 | 866 | 839±18 | [17] |
| | 8 | | | 730±55 | [24] |
| | 10 | 51 | 824 | 864±20 | [17] |
| | 10 | 65 | 829 | 803±20 | [17] |
| | 11 | 31 | 808 | 810±18 | [17] |
| | 11 | 53 | 813 | 670±30 | [22] |
| | 11 | 131 | 856 | 620±50 | [46] |
| | 11 | 133 | 857 | 876±18 | [17] |
| | 12 | 53 | 803 | 751±22 | [17] |
| | 12 | 133 | 846 | 670±40 | [23] |
| | 13 | 25 | 788 | 775±22 | [17] |
| | 13 | 53 | 794 | 752±24 | [17] |
| | 13 | 71 | 800 | 774±12 | [17] |
| | 13 | 133 | 836 | 160±20 | [46] |
| | 14 | 89 | 800 | 40±10 | [46] |
| $B0_u^+$ | 0 | 107 | 59 | 64±5 | [22] |
| | 0 | 179 | 61 | 75±4 | [22] |
| | 0 | | | 90±5 | [24] |
| | 2 | 71 | 59 | 80±3 | [17] |
| | 2 | 85 | 60 | 87±5 | [17] |
| | 3 | 66 | 60 | 83±1 | [17] |
| | 3 | 99 | 60 | 68±5 | [27] |
| | 4 | 65 | 61 | 76±1 | [17] |
| | 5 | 55 | 61 | 77±2 | [17] |
| | 5 | 103 | 62 | 57±3 | [27] |
| | 7 | 95 | 63 | 55±5 | [27] |
| | 8 | 71 | 63 | | |
| | 8 | | | 67.6±1.1 | [24] |
| | 9 | 71 | 64 | | |
| | 9 | | | 55.2±0.7 | |
| $B1_u$ | 2 | 86 | 100 | 107±7[a] | [18] |
| | 2 | 96 | 101 | 117±11[a] | [18] |
| | 4 | 52 | 106 | 49±4[a] | [18] |
| | 4 | 70 | 107 | 10±2[a] | [18] |

[a] Lifetime for the $1_u^-$ component.

Resulting *ab initio* transition moment functions $D_{\mu\nu}(r)$, along with empirical (RKR) potential-energy data, were used to evaluate radiative decay rates and lifetimes of excited $A0_u^+$, $B0_u^+$, and $B1_u$ states of $Te_2$. To avoid the direct summation over final vibrational levels without loss of accuracy, we employed the approximate sum rule of Tellinghuisen [41,42]. The necessary upper-state rovibrational wave func-

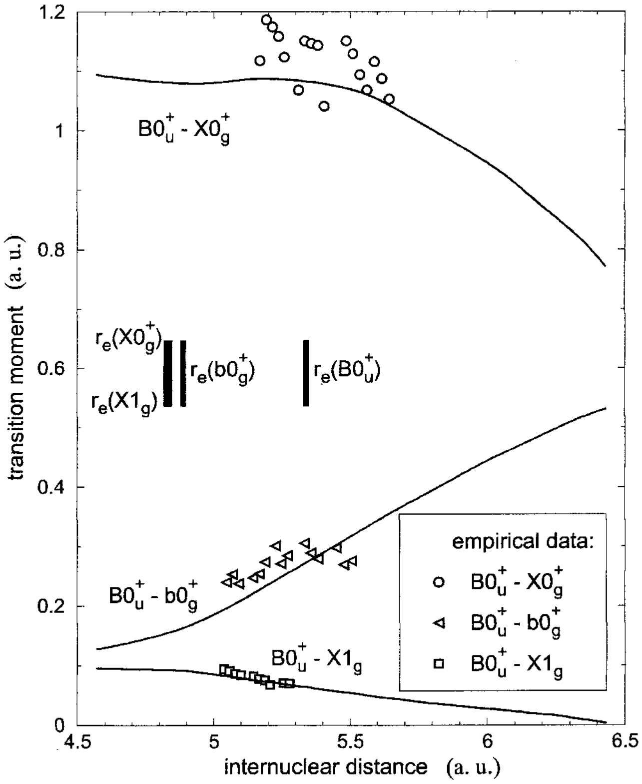

FIG. 4. *Ab initio* $B0_u^+ \rightarrow X0_g^+, X1_g, b0_g^+$ transition dipole moment functions (solid lines) and empirical transition moment estimates from Ref. [16].

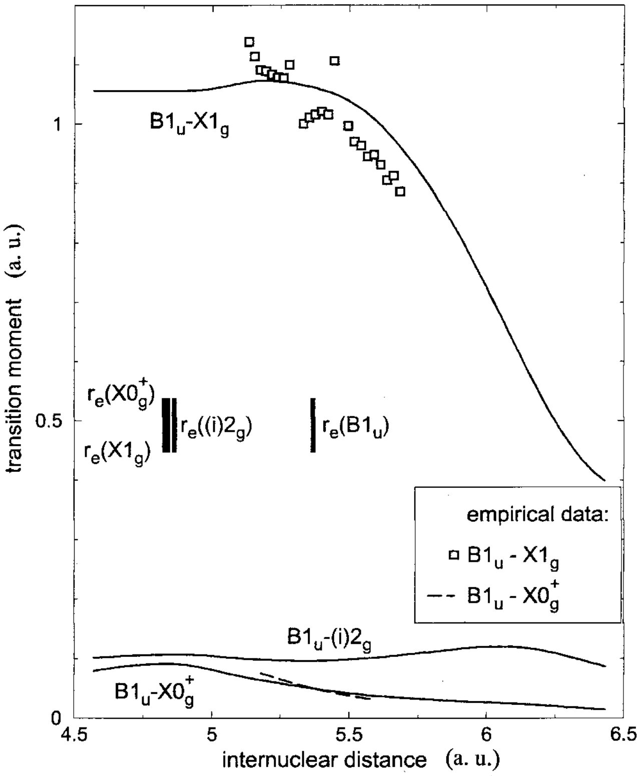

FIG. 5. *Ab initio* $B1_u^+ \rightarrow X0_g^+, X1_g, (i)2_g$ transition dipole moment functions (solid lines). Empirical data are taken from Refs. [16] and [18].

tions were computed by the VIBROT routine from the MOLCAS-3 program package [43].

## III. RESULTS AND DISCUSSION

Although both the REP and orbital basis sets employed in our work are suited to accurately describe electronic distributions and transition dipole moments rather than electronic energies, it might be of interest to estimate the reliability of the obtained transition energies as functions of the internuclear separation. Let us first notice that the present scheme ensures a reasonable description of low-lying atomic levels of Te correlating with the molecular states under study [the computed energies $E(\mathrm{Te}, {}^3P_1) = 4601\ \mathrm{cm}^{-1}$ and $E(\mathrm{Te}, {}^3P_0) = 4745\ \mathrm{cm}^{-1}$ should be compared with the experimental values 4751 and 4707 $\mathrm{cm}^{-1}$, respectively [44]]. Figure 1 presents the potential-energy functions for excited states of $\mathrm{Te}_2$ involved in the radiative decay of the $A0_u^+$, $B0_u^+$, and $B1_u$ states derived from the *ab initio* transition energies and accurate RKR ground-state potential [15]. These functions check well with their empirical counterparts [15,18,45] and give rise to reliable estimates of the main spectroscopic constants of $\mathrm{Te}_2$ (Table I). Note that for the $B0_u^+$ state solid and dashed lines in Fig. 1 are indistinguishable.

The calculated $A0_u^+ \rightarrow X0_g^+, X1_g, b0_g^+$ transition dipole moment functions required to describe the radiative decay of the $A0_u^+$ state are plotted in Fig. 2. Our results agree well with the relative values and $r$-centroid dependences of transition moments deduced from experimental spectral intensity distributions in Ref. [16]. Slight systematic deviations of absolute *ab initio* $D_{\mu\nu}$ values from their empirical counterparts disappear if one replaces the original normalization of empirical data based on the lifetime value $\tau(A0_u^+, v' = 11) = 670\ \mathrm{ns}$ [22] by that corresponding to a more recent experimental estimate $\tau(A0_u^+, v' = 11) = 844\ \mathrm{ns}$ [17].

The theoretical $A0_u^+, v' \rightarrow X0_g^+$ partial decay rates smoothly increase with $v'$, implying a similar behavior of the total $A0_u^+, v'$ radiative decay rates (Fig. 3). The corresponding radiative lifetimes for relatively small $v'$ and $J'$ are quite close to the experimental collisionless lifetimes (Table II). A striking discrepancy between the present radiative and measured total lifetimes for $v' > 13$ should be attributed to a strong predissociative decay. It is also highly probable that nonradiative intramolecular processes slightly shorten the measured lifetimes for the levels with $v'$ below 13, as well as for large angular momentum levels with any $v'$.

Figure 4 demonstrates reasonable agreement between the present *ab initio* and empirical $B0_u^+ \rightarrow X0_g^+, X1_g, b0_g^+$ transition moment functions. The $B0_u^+$ radiative decay is strongly dominated by the $B0_u^+ \rightarrow X0_g^+$ channel. In accordance with the experimental findings [17,18,27], the computed lifetimes (Table II) do not strongly depend on $v'$. Our estimates are slightly but systematically smaller than those reported in Ref. [17], demonstrating a better agreement with the results of Ferber *et al.* [22] and Klincare *et al.* [27]. It is difficult to judge the sources of disagreement between experimental $B0_u^+$ lifetimes presented in [17] and [22,27]. The $B0_u^+$-$B1_u^+$ mixing due to electron-rotation coupling, being the strongest for $v'=0,J'=107$ [18], tends to increase the lifetime of the $B0_u^+$ state. It is probably worth mentioning that all experiments in [22,27] were performed on fully spectrally resolved and unambiguously identified rotational lines.

The smallness of the computed $B1_u \rightarrow X0_g^+, b0_g^+, (i)2_g$ transition moments enables us to consider the radiative decay of the $B1_u$ state as a one-channel $B1_u \rightarrow X1_g$ process (see Fig. 5; the function corresponding to the very weak $B1_u \rightarrow b0_g^+$ transition $[D_{\mu\nu}(r_e(B1_u))=0.04\,\text{a.u.}]$ is not shown). The *ab initio* functions agree quite well with the available empirical dependences, and the theoretical estimates for $B1_u, v'=2$ lifetimes fairly reproduce the measured values (Table II). Note that the experimental lifetimes are presented for the $B1_u^-$ component, which, as opposed to $B1_u^+$, is not mixed with the $B0_u^+$ state. It is thus highly probable that the lifetime values for $v'=2$ are close to the spontaneous lifetimes; see the discussion in Ref. [19]. No catastrophic changes in theoretical radiative lifetimes occur in passing to higher vibrational levels; this allows us to conclude that the experimentally observed rapid decay of $B1_u, v'>2$ levels [19,27] should be explained by highly competitive nonradiative processes.

## IV. CONCLUSIONS

The dressed intermediate Hamiltonian concept is used to formulate a second-order perturbative quasirelativistic scheme of electronic structure and transition property calculations. The relativistic effects are introduced via core REP's and are restricted to an incomplete model space spanned by a numerically selected set of Slater determinants. The evaluation of effective model-space interactions arising from electrostatic couplings to the outer space takes advantage of the nonrelativistic symmetries, thus ensuring the computational simplicity of the scheme. The independent (fully uncontracted) determination of the contributions of the model-space determinants to the model wave functions by the final diagonalizaton offers the possibility to correctly describe the influence of the correlations on the spin-orbit interactions.

The method is applied to compute the transition dipole moment functions required for the description of the radiative decay of the $A0_u^+$, $B0_u^+$, and $B1_u$ states of $\text{Te}_2$. The results agree well with the empirical *r*-centroid dependences of transition moments derived from the experimental spectral intensity distributions [16,18]. The radiative lifetime estimates of low-lying rovibrational levels of the $A0_u^+$, $B0_u^+$, and $B1_u$ states of $^{130}\text{Te}_2$ deduced from our *ab initio* transition moment functions and RKR potential curves fairly reproduce the bulk of the corresponding experimental lifetime data. One can suppose that in some cases our scheme slightly overestimates the transition dipoles; this is quite natural for a low-order perturbative approximation that includes no renormalization terms. However, it should probably be noted that the level is reached when it is difficult to tell whether the experimental inaccuracies or drawbacks in the calculation scheme are responsible for the discrepancies between the estimated and observed radiative data. This suggests that the new challenge for experimentalists is to strive for more accurate and reliable data, which would allow us to test the theory experimentally. The decay of higher rovibrational levels is strongly affected by nonradiative processes. A quantitative theoretical study of such processes will demand a further improvement of relative electronic energy estimates. The necessary level of accuracy apparently can be achieved by a refinement of the shape-consistent REP model [47].

One of the main shortcomings of the described method, which can give rise to difficulties for the studies of the compounds of actinides and superheavy elements, consists in neglecting the repolarization of wave functions by the spin-orbit interactions between the model space and its orthogonal complement. These difficulties might be reduced by including the spin-orbit operator in the selection procedure (cf. [29,33]). It is also possible to partially incorporate the spin-orbit-dependent contributions into the intermediate Hamiltonian by means of the perturbation theory; however, this should give rise to rather tedious calculations in the relativistic (double group) symmetry.

## ACKNOWLEDGMENTS

A.Z. acknowledges financial support from the Russian Foundation for Basic Researches under the Grant No. 00-03-33004. R.F. acknowledges support from the Latvian Science Council under Grant No. 960323. We are indebted to Dr. A. V. Stolyarov (Moscow) and Dr. M. Tamanis (Riga) for useful discussions, as well as to Professor N. F. Stepanov (Moscow) for a critical reading of the manuscript.

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