Many-Body Theory Calculations of Positron Scattering and Annihilation in H_2, N_2, and CH_4

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The recently developed *ab initio* many-body theory of positron molecule binding [J. Hofierka *et al.*, Many-body theory of positron binding to polyatomic molecules, Nature (London) **606**, 688 (2022)] is combined with the shifted pseudostates method [A. R. Swann and G. F. Gribakin, Model-potential calculations of positron binding, scattering, and annihilation for atoms and small molecules using a Gaussian basis, Phys. Rev. A **101**, 022702 (2020)] to calculate positron scattering and annihilation rates on small molecules, namely H_2, N_2, and CH_4. The important effects of positron-molecule correlations are delineated. The method provides uniformly good results for annihilation rates on all the targets, from the simplest (H_2, for which only a sole previous calculation agrees with experiment), to larger targets, where high-quality calculations have not been available.

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Developing fundamental knowledge of positron scattering and annihilation in molecules is essential to, e.g., realize antimatter-based molecular spectroscopy [1–3] and next-generation antimatter traps [4–7], elucidate the process of molecular fragmentation [8–11], and properly understand how positrons propagate in and can act as probes of living tissue (relating to DNA damage and dosimetry in PET [12–17]), the Galaxy (e.g., to understand the galactic-center annihilation signal [18,19] and dark matter [20]), and materials [21–23].

The positron-molecule system is, however, characterized by strong positron-molecule correlations that are nonlocal and act over different length scales [24], and for molecules that bind the positron, spectacular resonance effects due to coupled electronic and vibrational dynamics [1]. They make the theoretical and computational description a challenging many-body problem. For positron scattering, R-matrix [25–29], Schwinger multichannel [30–37], Kohn variational [38–42], model potential [43,44], and convergent close coupling (CCC) [45,46] methods have been applied with considerable success to small molecules, including H_2, CH_4, N_2, CO_2, CO, allene, formamide, and pyrazine (see also [47]). Calculation of the positron-molecule annihilation rate—of chief interest in this Letter—is however, strikingly more difficult. For a gas of number density n_g the positron annihilation rate is parametrized as $\lambda = \pi r_0^2 c n_g Z_{\mathrm{eff}}$, where r_0 is the classical electron radius, c is the speed of light, and Z_{eff} is the effective number of electrons that participate in the annihilation process. Formally, Z_{eff} is equal to the electron density at the positron, $Z_{\mathrm{eff}} = \int \sum_{i=1}^{N_e} \delta(\boldsymbol{r}-\boldsymbol{r}_i)|\Psi_{\boldsymbol{k}}(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_{N_e},\boldsymbol{r})|^2 d\boldsymbol{r}_1 \ldots d\boldsymbol{r}_{N_e} d\boldsymbol{r}$, where $\Psi_{\boldsymbol{k}}$ is the total wave function of the system, with electron coordinates $\boldsymbol{r}_i$ and positron coordinate $\boldsymbol{r}$ [48]. It describes the scattering of a positron of momentum $\boldsymbol{k}$ by the molecule, and is normalized asymptotically to the product of the ground-state target molecular wave function and positron plane wave. Accurate calculation of Z_{eff} thus requires proper account of the scattering dynamics and positron-molecule correlations, including short-range electron-positron interactions. Even for the simplest molecule, H_2, calculations of Z_{eff} via sophisticated methods, including R-matrix [27] and the Kohn variational [41,49] and Schwinger multichannel methods [50], disagree, all substantially underestimating experiment [51–53] (by $\sim 15\% - 50\%$), to which only a stochastic variational method (SVM) calculation [54] is compatible. For N_2, used ubiquitously as a buffer gas in positron traps [4,5], the Schwinger multichannel method (the only *ab initio* calculation we are aware of) underestimates experiment by a factor of > 3. Moreover, these methods cannot be easily scaled to larger molecules. Theoretical developments are demanded.

Many-body theory (MBT) is a powerful method that can accurately account for strong positron and electron correlations with atoms, molecules, and ions (see, e.g., [22,55–69]). For atoms, a B-spline implementation provided a complete *ab initio* description of positron scattering, annihilation, and

cooling [64,65,69–71] and positronium (Ps) "pickoff" annihilation [72] in (noble gas) atoms. Most recently, we developed and successfully applied a multicentered Bethe-Salpeter Gaussian-orbital-based many-body approach to positron binding in molecules, implemented in our EXCITON+ code [24].

Here, we extend the approach beyond binding, combining it with the recently devised shifted-pseudostate-normalization method of [44] to perform fixed-nuclei [73] calculations of low-energy positron scattering and annihilation rates on the same footing for the small molecules H_2, N_2, and CH_4. We quantify the effects of positron-molecule correlations, including positron-induced polarization, screening, and virtual-positronium (virtual-Ps) and positron-hole interactions, and compare with experiment and theory where available. For the annihilation rates, we find excellent agreement with the benchmark SVM calculation [54,74] and experiment for H_2, providing a consensus, and overall good agreement with experiment for N_2 and CH_4.

Theory and numerical implementation.—The positron (quasiparticle) wave function ψ_ε in the field of a many-electron target is found from the following Dyson equation [24,75]:

$$(H^{(0)} + \hat{\Sigma}_\varepsilon)\psi_\varepsilon(\boldsymbol{r}) = \varepsilon\psi_\varepsilon(\boldsymbol{r}). \tag{1}$$

Here, $H^{(0)}$ is the zeroth-order Hamiltonian, which we take to be that of the positron in the Hartree-Fock (HF) field of the ground-state molecule, and $\hat{\Sigma}_\varepsilon$ is the nonlocal, energy-dependent correlation potential (self-energy, an optical potential for elastic scattering [76]). In practice we calculate the matrix elements of Σ via its diagrammatic expansion in the residual electron-electron and electron-positron interactions [77]. See Ref. [24] for full details. Briefly, we include three classes of infinite series in the expansion: Fig. 1(a), the "GW" diagram [the product of the positron Green's function G and the screened Coulomb interaction W, which we calculate at the Bethe-Salpeter equation (BSE) level], describes the positron-induced polarization of the molecular electron cloud, the screening of it by the molecular electrons, and electron-hole attractions; Fig. 1(b), the electron-positron ladder series ("Γ block"), describes the nonperturbative virtual-Ps formation process; and Fig. 1(c), the positron-hole ladder series ("Λ block").

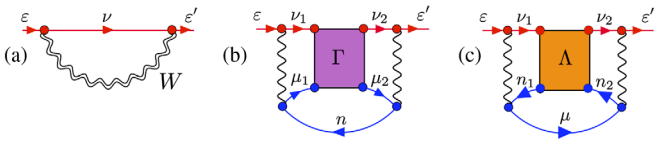

FIG. 1. The main contributions to the positron-molecule self-energy: (a) the GW diagram; (b), (c) the infinite ladder series of electron-positron interactions (virtual-Ps formation "Γ block") and positron-hole interactions ("Λ block"). Lines labeled ν (μ) [n] are excited positron (electron) [hole] propagators; a single (double) wavy line denotes a bare (dressed) Coulomb interaction. See text and extended data, Fig. 1 of [24], for full details.

We expand the electron and positron states in Gaussian basis sets (see below), transforming Eq. (1) into a linear matrix equation. For a target that has no bound states for the positron, its solution yields a set of n discrete positron continuum pseudostates and their corresponding energies ε_n ($n = 1, 2, \ldots$). These pseudostates decay exponentially rather than oscillate at large positron-target separations, and are normalized to unity instead of to an asymptotic plane wave as required by a true continuum state. Moreover, the lack of spherical symmetry of the multicentered target means that the orbital angular momentum is not conserved. However, at low positron momenta ($kR_a \ll 1$, where R_a is the radius of the target), the mixing between partial waves due to the noncentral nature of the potential is small or negligible, and one can identify (approximately) states with eigenvalues of the squared orbital angular momentum operator L^2 close to zero (s states), which are expected to dominate the scattering and annihilation. In this case we can obtain the appropriate normalization following [44], comparing the energies of (approximate) s states against corresponding free positron pseudostate energies $\varepsilon_n^{(0)}$ (found by setting H_0 equal to the positron kinetic energy). We thus calculate the s-wave phase shift for a positron of energy ε_n as $\delta_0 = [n - f^{-1}(\varepsilon_n)]\pi$, where n is the number of the s-wave pseudostate, and $f(n)$ is a function of a continuous variable n satisfying $f(n) = \varepsilon_n^{(0)}$ [44]. We use the same procedure for p and d waves. Moreover, we make use of the shifted energies to approximate the annihilation rate as $Z_{\rm eff} = 4\pi\delta_{ep}A^{-2}$, with normalization $A^2 = (2\ell+1)^{-1}2\sqrt{2\epsilon}d\epsilon/dn$ [44], where ℓ is the angular momenta, and $\delta_{\rm ep} = 2\sum_{i=1}^{N_e/2}\gamma_i\int|\varphi_i(\boldsymbol{r})|^2|\psi(\boldsymbol{r})|^2d\tau$ is the annihilation contact density summed over all occupied electronic molecular orbitals (MOs) φ_i, including vertex enhancement factors (in a.u.) $\gamma_i = 1 + \sqrt{1.31/|\varepsilon_i|} + (0.834/|\varepsilon_i|)^{2.15}$ for MO i with energy ε_i that account for short-range electron-positron attraction [65,69].

We implement the above in our EXCITON+ Gaussian-basis code [24] using aug-cc-pVXZ (X = T or Q) basis sets on the atoms of the molecule and up to 20 "ghost" centers away from the molecule to describe virtual-Ps formation, and a 19s17p16d15f even-tempered set on the molecular center to help describe the long-range interactions; we assessed convergence and sensitivity to bond lengths [see Supplemental Material (SM) for full details [78]].

Results: Effect of many-body correlations.—Figure 2 shows the phase shifts and normalized annihilation rate $Z_{\rm eff}$ for H_2 (representative of the three molecules considered) calculated at the HF, $\Sigma^{(2)}$, GW, $GW + \Gamma$, and $GW + \Gamma + \Lambda$ level for the correlation potential (see Fig. 1). At the HF level the positron-molecule interaction is repulsive (corresponding to a negative phase shift, and small electron-positron overlap and thus annihilation rate); including the

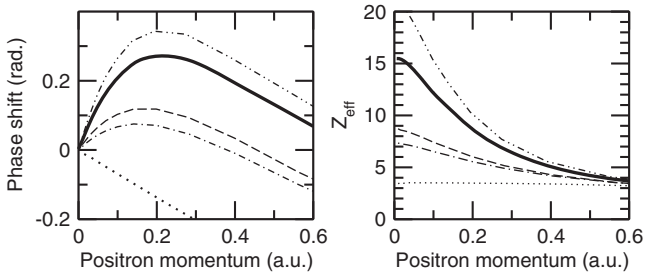

FIG. 2. The effects of positron-molecule many-body correlations shown via the calculated s-wave scattering phase shift (left) and normalized annihilation rate Z_{eff} (right) for H_2 (representative of the three molecules considered in this Letter) in different approximations to the positron-molecule self-energy (see Fig. 1): HF (black dotted), bare polarization $\Sigma^{(2)}$ (black dot-dashed), GW (black dashed), $GW+\Gamma$ (black dot-dot-dashed), and $GW+\Gamma+\Lambda$ (solid line).

bare polarization $\Sigma^{(2)}$ [85] produces an attractive interaction at low momenta (turning the phase shift positive and increasing the electron-positron overlap and thus Z_{eff}), which is further enhanced by the inclusion of the dressed ring diagrams of the GW@BSE, i.e., the intra-ring BSE electron-hole attractions are larger than the repulsive screening effects from the random-phase approximation ring series. The additional inclusion of the virtual-Ps contribution ($GW+\Gamma$) further increases the attractive potential substantially, causing a factor of $\sim$3 increase in the phase shift maximum and a more than doubling of Z_{eff} at low momenta, but is tempered by the repulsive positron-hole (Λ-block) contribution. See SM, Fig. 3, for the corresponding graphs for N_2 and CH_4.

Scattering.—Figure 3 shows the calculated elastic cross sections compared with other theory and measurements. Also see SM, Table I, for calculated scattering lengths determined from fits of the effective-range-theory expansion to the phase shifts, and from the momentum dependence of the annihilation rate. There is little consensus between the various theory and experiment. For H_2, for which our calculated annihilation rate is in excellent agreement with the SVM (see below), our calculated cross section is noticeably larger than the CCC calculation [46] (which is optimized for H_2 and expected to be accurate) and lies within the error bar of the Trento [86] and ANU [89] measurements only around $\sim 2-5$ eV. Our calculated scattering length is, however, within $\lesssim$15% of the CCC and SVM result, and to $\lesssim$5% as determined from the momentum dependence of the annihilation rate (see below). For N_2 our result is in good agreement with the model potential (s-wave) calculation of [44] at low energies (which gives Z_{eff} in good agreement with experiment), and compatible with the measurements of Zecca *et al.* [87] below $\sim$1 eV but noticeably larger beyond this. For CH_4 our results are consistent with the measurements of Zecca *et al.* [34] only at $\sim$1 eV, but are considerably larger at low energies, where they are compatible with the model potential result [44] that gives Z_{eff} in agreement with experiment.

Annihilation rate Z_{eff}.—Of chief interest in this work is the annihilation rate Z_{eff} due to the challenge it poses for theory and lack of accurate methods. Figure 4 shows our normalized annihilation rate $Z_{\mathrm{eff}}(k)$ as a function of positron momentum calculated in our most sophisticated approximation ($GW+\Gamma+\Lambda$ self-energy and including vertex enhancement factors). For the s wave, we show the discrete data points calculated along with fits to the physically motivated form [64] $Z_{\mathrm{eff}}(k)=F/(\kappa^2+k^2+Ak^4)+B$ where F, κ, A, and B are constants (see SM, Table II,

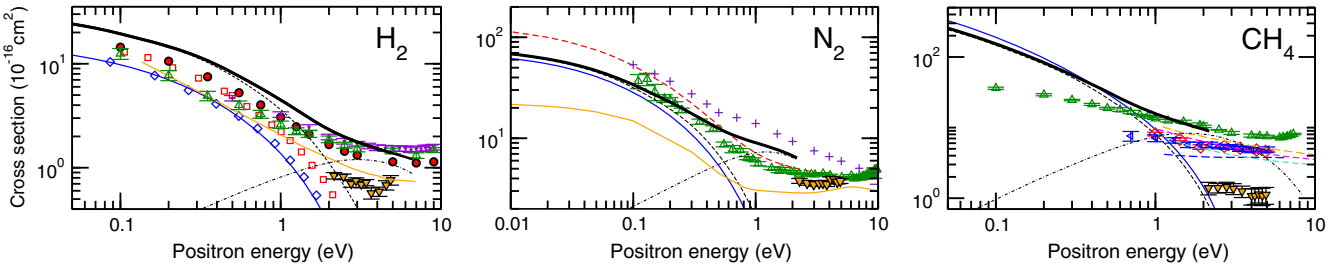

FIG. 3. MBT calculated scattering cross sections for H_2, N_2, and CH_4: s wave (thin dashed black line), p wave (thin dash-dotted black line), and $s+p+d$ total (thick solid black line) for bond lengths of $R=1.45$, 2.014, and 2.06 a.u. for H_2, N_2, and the C—H bond in CH_4. Also shown are measurements by Zecca *et al.* [34,86,87] (green triangles) and Charlton *et al.* [88] (orange triangles), and recent model potential calculations of Swann and Gribakin [44] (blue solid line) for each molecule; and additionally for H_2 the measurements of Machacek *et al.* (purple triangles) [89], Schwinger multichannel [90] (orange line), Kohn variational [40] (blue diamonds), convergent close coupling [46] (red filled circles) calculations, and modified-effective-range-theory fit of measured cross sections [91] (red squares); for N_2, the Schwinger multichannel [32] (orange line), local-complex-potential [92] (plus symbols), and correlation-polarization-model [93] (dashed red) calculations; and for CH_4, correlation-polarization-model-potential calculations of Franz [94] (orange dashed line), Jain and Gianturco [95] (blue dashed line), and Dibyendu *et al.* [96] (magenta dashed line), Schwinger multichannel [34] (turquoise dashed), and measurements of Sueoka and Mori [97] (blue triangle) and Dababneh *et al.* [98] (red diamonds).

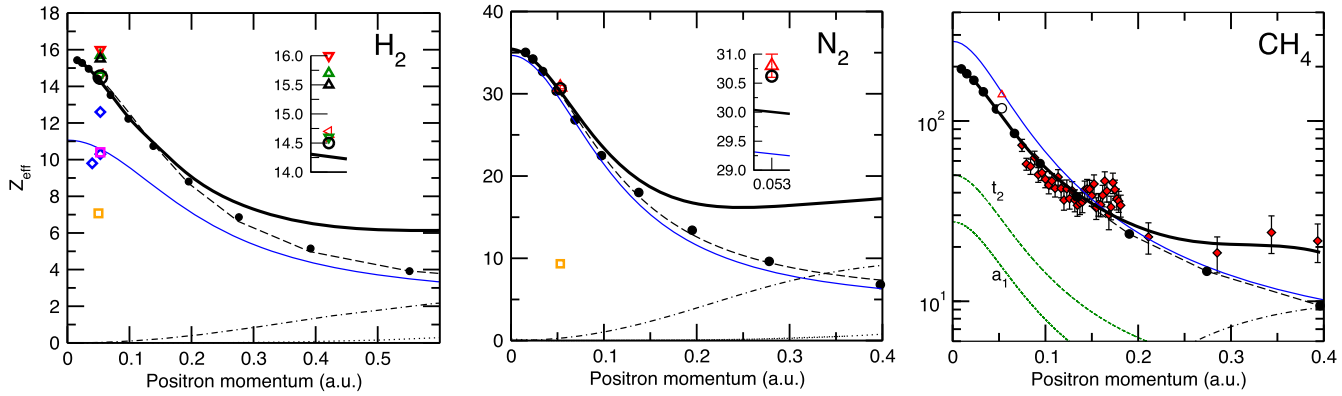

FIG. 4. MBT calculated annihilation rate $Z_{\mathrm{eff}}(k)$ for H_2, N_2, and CH_4: s wave (thin dashed black line), p wave (thin dashed-dotted), d wave (dotted), and total $s+p+d$ (thick solid black line). Results are shown for bond lengths of $R = 1.4$, 2.014, and 2.06 a.u. for H_2, N_2, and the C-H bond in CH_4. Also shown are the room-temperature Maxwellian averaged $\bar{Z}_{\mathrm{eff}}$ from our calculation (black open circle; for H_2 black triangle up is for $R = 1.45$ a.u. for comparison) and experiment (red triangles) for H_2 [51,52,99], N_2 [53], and CH_4 [53], along with energy-resolved measurements for CH_4 [100] (red diamonds), the recent model potential calculations of [44] (solid blue line). Additionally for H_2, the calculated room-temperature values from the Kohn variational method (blue diamonds) [41,49,101], molecular R-matrix (magenta square) [27], and SVM at bond length of $R = 1.4$ a.u. (green triangle down) and $R = 1.45$ a.u. (green triangle up) [74], and the Schwinger multichannel method at $k = 0.05$ a.u. (orange squares) [32,50]. The latter is also shown for N_2. For CH_4 we also show the individual s-wave contributions from the $2a_1$ and one of the triply degenerate t_2 highest occupied molecular orbitals (HOMOs).

for their values). We also show the calculated room-temperature Maxwellian average (open circle) $\bar{Z}_{\mathrm{eff}} = (2\pi k_B T)^{-3/2} \int_0^\infty Z_{\mathrm{eff}}(k) \exp(-k^2/2k_B T) 4\pi k^2 dk$. Table I gives the values of $\bar{Z}_{\mathrm{eff}}$: for H_2 and N_2 (CH_4), we found it to be $< 1\%$ (10%) larger than $Z_{\mathrm{eff}}(k)$ at thermal $k \sim 0.05$ a.u.

TABLE I. Maxwellian-averaged annihilation rate $\bar{Z}_{\mathrm{eff}}$.

	H_2	N_2	CH_4
Present MBT[a]	14.5, 15.5[b]	30.6[c]	118[d]
SMC[e] [32,50]	7.70	8.96	⋯
R-matrix [27]	10.4	⋯	⋯
Kohn var. [41,49]	12.6[f]	⋯	⋯
SVM [102]	14.6, 15.7[b]	⋯	⋯
Corr. pol. [103,104]	⋯	44 ± 4	99.5[g]
LCAO[h] [105]	14.6	⋯	⋯
Model pot. [44]	10.6	29.8	163
Experiment	14.7 ± 0.2 [99]	30.8 ± 0.2 [53]	140 ± 0.8 [53]
	16.0 ± 0.2 [51,53][i]		
	14.6 ± 0.1 [52]		

[a]Positron-molecule self-energy at $GW + \Gamma + \Lambda$ [Figs. 1(a)–1(c)].
[b]H_2 calculation using bond lengths of $R = 1.40$ a.u., $R = 1.45$ a.u.
[c]N_2 calculation using bond lengths of $R = 2.014$ a.u.
[d]CH_4 calculation using C—H bond length of $R = 2.06$ a.u.
[e]Schwinger multichannel method at $k = 0.05$ a.u.
[f]Kohn variational "method of models" calculation.
[g]Correlation polarization potential calculations.
[h]Linear combination of atomic orbital with correlation adjustment factors.
[i]Ref. [53] recommended value.

Considering comparison with other theory and experiment, for H_2 a number of sophisticated calculations of Z_{eff}, namely the Schwinger variational (7.7), R-matrix (10.4), and Kohn variational (12.6), are in considerable disagreement, and moreover, all substantially underestimated experiment (14.6–16 [51–53,99], with 16 the recommended value [53]). The only compatible calculation to date is the SVM calculation of Zhang and Mitroy [54] (14.6 for a bond length of $R = 1.4$ a.u., and 15.7 for a bond length of $R = 1.45$ a.u.). Our respective results of 14.5 and 15.5 are in excellent agreement with this and experiment, providing a consensus, and demonstrate that the MBT accurately describes the correlations. The scattering length determined from $Z_{\mathrm{eff}}(k)$ as $a \sim 1/2\kappa = -2.73$ a.u. agrees to $\lesssim 3\%$ of the CCC and SVM calculations (see SM, Table I).

For N_2, the only *ab initio* calculation we are aware of is the Schwinger multichannel calculation, which finds $Z_{\mathrm{eff}} = 8.96$ [32,50], compared to the recommended measured value of 30.8 ± 0.2 [53]. In contrast, our calculated value of 30.6 is in excellent agreement with experiment, indicating proper account of the correlations that act to enhance Z_{eff}, and with the recent model potential calculation [44]. We found that a 2% increase in the bond length leads to a ∼5% increase of $\bar{Z}_{\mathrm{eff}}$. We found that the fractional contribution to the s-wave Z_{eff} from the highest 5 MOs $a_{1g}a_{2u}a_{1g}2e_u$ of HF ionization energies 40.67 eV, 20.91 eV, 17.34 eV, 17.10 eV, and 17.10 eV to be 0.06, 0.24, 0.28, 0.21, and 0.21, respectively, i.e., a non-negligible fraction of annihilation occurs on MOs below the HOMO due to their favorable overlap with the positron wave function that is maximum

around the N atoms. This pattern was observed for bound states [24] and in the extensive fragmentation patterns [8–11] of polyatomic molecules.

For CH_4, we find good overall agreement with the positron-momentum-dependent $Z_{\rm eff}(k)$ measurements of Marler *et al.* [100] across the full momentum range including at $k \sim 0.4$ a.u. where the p wave contributes, except for the region around 0.17 a.u, which is close to two vibrational modes [48].

Our thermalized value $\bar{Z}_{\rm eff} = 118$ is lower than the measurement 140 ± 0.8 [51,53], and the model potential calculation [44] (which uses adjustable parameters), especially at small k. We found the fractional contribution from the $1a_1$, $2a_1$, and each of the t_2 orbitals, of ionization energies 304.92 eV, 25.66 eV, 14.83 eV, to be 0.0025, 0.15, 0.281. The large scattering length in CH_4 makes $\bar{Z}_{\rm eff}$ very sensitive to the correlation potential strength at low momenta (since $\kappa \sim 1/2a \ll 1$). We assessed convergence of the basis set, increasing from 12 to 20 ghosts, and from aug-cc-pVTZ to aug-cc-pVQZ functions, finding only a 5% increase (see SM, Fig. 2). We include angular momenta functions up to $\ell = 4$: while the basis functions from different centers combine to provide effectively higher angular momenta [106], this may be insufficient to converge the virtual-Ps diagram [107]. Moreover, the annihilation-vertex enhancement factors (determined from *ab initio* calculations for atoms [65,69]) may underestimate the true short-range enhancement for delocalized MOs, especially since the positron can probe electron density in interstitial regions where nuclear repulsion is reduced [108]. Calculation of the vertex enhancement for molecules is challenging, and beyond the scope of this work. Further theoretical and experimental work on CH_4 is warranted.

Summary and outlook.—The accurate *ab initio* calculation of the positron-molecule annihilation rate has proven to be a challenging problem, thwarting the efforts of quantum chemistry methods for all but the simplest molecule, H_2, for which only a sole (SVM) calculation agrees with experiment. In this work, many-body theory was developed and applied to calculate positron scattering properties and annihilation rates, on the same footing, in H_2, N_2, and CH_4. The effects of correlations were elucidated. For the annihilation rates $Z_{\rm eff}$, for H_2, the power of the approach was demonstrated by the excellent agreement with the benchmark SVM result, thus providing a consensus with experiment. Moreover, overall good agreement with experiment was found for N_2 and CH_4 (though further theoretical and experimental work on the latter was called for). Importantly, the method is systematically improvable via the inclusion of additional higher-order diagrams or via coupling of the diagrams in Fig. 1 [111], and/or by dressing the electron propagators for a self-consistent determination of the molecular properties. The positron-molecule correlation potential the many-body approach provides can be incorporated in a T-matrix (see e.g., [59,112–115]) or Schwinger multichannel [30–37] approach to enable calculations on larger molecules, and should provide uniform accuracy. Moreover, its calculation is an essential starting point to enable a many-body description of annihilation γ spectra, and of inelastic processes [59,116,117] relevant to resonant interactions in positron-binding molecules [1].

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